QUARTERLY REVIEWS

THE KINETICS OF CRYSTAL GROWTH

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Introduction

CRYSTALLISATION is a term which is used to characterise a number of phenomena. The formation of a solid phase in solution, melt, or vapour, and polymorphic transformations in solid phases are some of the extensively studied fields. The present Review is not intended to be exhaustive but rather to show developments which have taken place in the study of the kinetics of crystal growth from condensed phases.

The process of crystallisation was used for the purification of substances as far back as the 8th Century. Early in the 18th Century, Fahrenheit discovered that water could be successfully supercooled without the formation of ice crystals and that extraneous factors such as shock would induce crystallisation. Many other workers during the 18th and 19th Centuries studied this phenomenon, and qualitative data were obtained to show that it is possible to exceed the normal solubility of a salt in solution without crystallisation taking place. The average life of a supersaturated solution was considered, and also the size of a "critical" nucleus just capable of growing in such a solution. In 1872, de Coppet[1] produced evidence to show that the average life of a supersaturated solution was inversely proportional to the degree of supersaturation. Experimenting with hydrates of sodium sulphate, he argued that any supersaturated solution would crystallise spontaneously, if given sufficient time. During this period, large numbers of postulates, often applying to only one crystallising system, tended to produce a confusion of disconnected facts, and it was not until 1897 with the work of Ostwald[2] that the problem began to be resolved. In a series of ingenious experiments designed to estimate the effective size of a nucleating crystal, Ostwald discovered that for sodium chlorate a mass of 10^{-10}g. was indicated. He recognised that this was only an upper limiting value but nevertheless it was the beginning of a series of studies which are still being pursued.

One of Ostwald's main contributions was his continued support for the idea of a metastable limit[3] in the concentration, at which there was a transition from stable to unstable supersaturation. He recognised the importance of some of Gibbs's fundamental contributions on thermodynamic stability

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[1] de Coppet, *Bull. soc. chim. France*, 1872, **17**, 146.

[2] Ostwald, *Z. phys. Chem.*, 1897, **22**, 289; **23**, 365; 1900, **34**, 444.

[3] Volmer, "Kinetik der Phasenbildung," Edwards Bros., Ann Arbor, Michigan, 1945.

and metastable states, and many of his original concepts form the basis of modern theories of crystal growth. Recent approaches to the problem, which will be discussed later, are of two types; one is based upon theoretical work on formation of the nucleus, and the other upon experimental observations of the results of mixing two reactant solutions to form the supersaturated solution.

Experimental Methods

In principle, the experimental methods used for studying crystallisation are very simple. Much qualitative work has been done by preparing supersaturated solutions and observing the visible onset of crystallisation. Such experiments cannot be expected to yield reproducible results and, moreover, they give no information as to the size and size distribution of the crystallites.

Crystallisation and dissolution may be studied either by[1] observing changes in the crystals themselves, or in the composition of the nutrient medium. In the former, the change in linear dimensions of the crystal or in the area of individual faces may be determined microscopically.[4] Wagner[5] measured the rate of dissolution of sodium chloride simply by following the loss in weight with a spring balance. Using the theory of layer growth, Sears[6] measured the rate of advance of a layer edge and its thickness, and expressed growth as the product of these parameters. It is important to ensure in all these experiments that the crystal habit does not change during growth. Again, it is possible to observe the velocity of "linear" crystallisation when a supersaturated solution, contained in a capillary tube, is inoculated with seed crystals at one end. This velocity has no crystallographic meaning, since it is influenced by the velocities of nucleation and of growth of all the crystal faces, the dissipation of the heat of crystallisation, and restriction of the container. Nevertheless, it is fairly reproducible under controlled conditions, and attempts have been made to relate it to theories of crystal growth.[7]

In following the course of crystallisation by changes in the nutrient medium, extensive use has been made of interferometry which is capable of yielding values for concentrations close to crystal faces.[8] Turbidimetry and dilatometry are also useful[9] and, if the crystallites are monodisperse, determination of the transmittance and scattering of monochromatic ultraviolet light as a function of angle gives a simple means of determining the size and number of particles.[10] Solution concentrations may be

[4] Morris and Strickland-Constable, *Trans. Faraday Soc.*, 1954, **50**, 1378.
[5] Wagner, *J. Phys. Colloid Chem.*, 1949, **53**, 1030.
[6] Sears, *J. Chem. Phys.*, 1956, **24**, 868; **25**, 637.
[7] Chatterji and Rastogi, *J. Phys. Chem.*, 1955, **59**, 1.
[8] Humphreys-Owen, *Proc. Roy. Soc.*, 1949, *A*, **197**, 218.
[9] Allen, *J. Phys. Chem.*, 1953, **57**, 715.
[10] Kenyon and La Mer, *J. Colloid Sci.*, 1949, **4**, 163.

measured rapidly by precise conductometric[11] and potentiometric[12] methods, as well as with radioactive tracers.[13] Heubel and Devrainne[14] determined the heat changes during crystallisation and were able to calculate the surface area and mass of salt precipitated.

Nucleation

The formation of crystals in liquid or solid systems, and of liquid in vapour systems, takes place in two steps. The first, nucleation, corresponds to the production of new centres from which spontaneous growth or condensation can occur. In the second, these first particles grow as material from the nutrient medium is deposited on them. The concepts underlying the first of these steps as they apply to solutions are best understood by employing the analogy of the condensation of a vapour for which the classical theories of nucleation were developed. These have been reviewed by Bradley[15] and others.[16] In the formation of nuclei in solution there are a number of additional complicating factors such as diffusion, solvation of solute ions and desolvation on crystallising, surface adsorption, and double-layer formation. Nevertheless, it is the nucleation process which determines the size and size distribution of the crystals of precipitate produced, and this is a factor of supreme importance in analytical procedures.

As the concentration of a solution is increased, the new phase, although thermodynamically stable, is not formed until a considerable degree of supersaturation has been achieved. The energy barrier which must be surmounted before stable nuclei will form is due to the surface energy of these minute particles. The decrease in free energy in transferring solute from its more unstable state in the supersaturated solution to the new phase is counterbalanced by the increase in surface free energy of the nucleus. Once formed, the nuclei are capable of growing until final equilibrium is reached in the second or growth stage.

The Steady-state Approach.—By analogy with the condensation of a vapour, we may imagine that statistical fluctuations within a supersaturated system give rise to relatively short-lived clusters formed by stepwise aggregation involving single ions or molecules X:

$$\begin{aligned} X + X &\rightleftharpoons X_2 \\ X_2 + X &\rightleftharpoons X_3 \\ \\ X_{j-1} + X &\rightleftharpoons X_j \\ X_j + X &\rightleftharpoons X_{j+1} \end{aligned} \qquad (1)$$

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[11] Davies and Jones, *Discuss, Faraday Soc.*, 1949, **5**, 103.
[12] Van Hook, *J. Phys. Chem.*, 1940, **44**, 751.
[13] Enüstün and Turkevich, *J. Amer. Chem. Soc.*, 1960, **82**, 4502.
[14] Heubel and Devrainne, *Compt. rend.*, 1961, **252**, 1158.
[15] Bradley, *Quart. Rev.*, 1951, **5**, 315.
[16] Dunning, "Chemistry of the Solid State," ed. Garner, Butterworths, London, 1955.

These aggregates may be considered to be minute spherical droplets to which we may apply the Kelvin–Gibbs equation,

$$r_j = (2\,\sigma\, v/\boldsymbol{R}T)\ln p_j/p_0, \tag{2}$$

where p_j is the vapour pressure of a droplet of radius r_j containing j molecules, p_0 the vapour pressure of the plane liquid surface, σ the surface tension of the droplet, and v the molal volume of the liquid. In precipitation from condensed phases, p_j/p_0 can be expressed as a concentration ratio m/m_0, where m_0 is the solubility value. Assuming that X_j represents the nucleus of critical size, just capable of growing, smaller clusters will tend to dissociate rather than to grow since growth requires work to extend the surface area. Dissociation, however, is opposed by the tendency of the supersaturated solution to deplete itself. Clusters larger than X_j will thus tend to grow, since the surface-energy term becomes less important as size increases. Once the critical size has been reached, by aggregation, the supersaturation collapses.

For the calculation of the frequency of nucleation Volmer[17] assumed a state of quasi-equilibrium in which the distribution of embryos of all sizes up to X_j was stationary with time. This assumption is valid provided that the subsequent growth rate is small enough not to disturb the statistical distribution.

$$\text{Writing } {}_j\mathrm{X} \rightleftharpoons \mathrm{X}_j,$$

the Law of Mass Action gives

$$\Delta G_j^\circ = \boldsymbol{k}T\ln\{\mathrm{X}_j\}/\{\mathrm{X}\}^j,$$

where ΔG_j° is the standard free energy of formation of a j-cluster from j single molecules, and braces enclose activities. The chemical potential of a single molecule is given by,

$$\mu_1 = \mu_1^\circ + \boldsymbol{k}T\ln\{\mathrm{X}\},$$

and of a j-cluster by,

$$\mu_j = \mu^\circ + \boldsymbol{k}T\ln\{\mathrm{X}_j\},$$

and so $\Delta G_j^\circ = \mu_j^\circ - j\mu_1^\circ$.

The free energy of j molecules in the newly formed phase is $j\mu_{\mathrm{S}}$, where

$$\mu_{\mathrm{S}} = \mu_1^\circ + \boldsymbol{k}T\ln\{\mathrm{X}_0\},$$

and $\{\mathrm{X}_0\}$ is the activity at saturation. When a spherical nucleus of radius r is separated from the bulk liquid, the free-energy of formation will also contain a surface contribution $4\pi r^2\sigma$. The free-energy of formation of the nucleus at rest may thus be written

$$\Delta G_j \sim \Delta G_j^\circ = j(\mu_{\mathrm{S}} - \mu_1) + 4\pi r^2\sigma$$

$$\text{or } \Delta G_j = -\frac{4\pi}{3}\frac{r^3}{v}\boldsymbol{k}T\ln\alpha + 4\pi r^2\sigma \tag{3}$$

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[17] Volmer, "Kinetik der Phasenbildung," Edwards Bros., Ann Arbor, Michigan 1945.

where α is the supersaturation ($= \{X\}/\{X_0\}$). The size of the critical nucleus is that which corresponds to a maximum in free energy, ΔG_C, and from eqn. (2) is

$$r_C = 2\sigma v/kT \ln \alpha$$

at which $\Delta G_C = 16\pi\sigma^3 v^2/[3(kT \ln \alpha)^2]$ (4)

In accordance with current rate theory, the rate at which the critical nuclei form is therefore

$$J = A \exp\left(-\frac{\Delta G_C}{kT}\right) = A \exp\left[-\frac{16\pi\sigma^3 v^2}{3k^3T^3 (\ln \alpha)^2}\right] \tag{5}$$

The pre-exponential term A has been discussed in the theories of Becker and Döring[18] and others,[15] who used the kinetic theory to calculate the rate of condensation on to the embryo. The very rapid increase in nucleation rate predicted by eqn. (5) as the supersaturation increases has been substantiated by experimental observations on the condensation of vapours using cloud-chamber techniques. Higuchi and O'Konski[19] have recently developed a more elegant method for studying nucleation kinetics involving steady-state production of nuclei in a turbulent jet. A dilute vapour issuing from a nozzle was rapidly quenched by a cooler annular gas stream, and the resulting aerosol particles were electronically counted by means of light-scattering instrumentation. The agreement between experimental kinetic factors A and those calculated from the Becker–Döring theory was very good for some systems such as the condensation of dibutyl phthalate vapour. Deviations for substances such as triethylene glycol were attributed to the greater hydrogen bonding involved or to the lower number of molecules in the critical nucleus. There are of course other complicating factors, such as heterogeneous nucleation, which make interpretation of the results difficult.

We are not specifically concerned in this Review with the theories developed for the condensation of vapours. Turnbull[20] has proposed, for the nucleation of barium sulphate in solution, a pre-exponential term

$$A = n\nu \exp(-\Delta G_a/kT) \tag{6}$$

where n is the number of Ba^{2+} and SO_4^{2-} ions/unit vol., ν the number of fruitful encounters or the "jump" frequency, and ΔG_a the free-energy of activation for growth of the crystals. ΔG_a is not well defined since it involves a number of characteristic activation energies corresponding to diffusion and a variety of surface processes. The structure of the nucleus is not known but the surface energy will vary from plane to plane. The contributions made by edges and corners may be a significant part of the whole and so calculation of the rate of nucleation by eqns. (5) and (6) is very difficult.

[18] Becker and Döring, *Ann. Physik*, 1935, **24**, 719.
[19] Higuchi and O'Konski, *J. Colloid Sci.*, 1960, **15**, 14.
[20] Turnbull, *Acta Metallurgica*, 1953, **1**, 684.

Induction Effects in Nucleation.—An imperfection of the theory lies in its assumption of steady-state conditions. These may only be applied if the supersaturation is built up homogeneously and very slowly until the critical value is reached. The steady-state concentrations of clusters of various sizes will then always be present. In many cases, there is a measurable time interval or induction period between the production of supersaturation and the onset of precipitation even though immediate nucleation is predicted by the Becker–Döring theory. It has been shown[21] that such delays in nucleation may be anticipated on the basis of the time required for attainment of steady-state conditions. The calculation of the induction time is extremely difficult, however, and different workers have introduced different simplifying assumptions.

A straightforward kinetic approach was adopted by Christiansen and Nielsen[21] for crystallisation from solution. They considered that the induction period was the time required to build up clusters of size X_p by a steady-state process, all of the preceding steps being in a quasi-equilibrium state. X_p was assumed to be different from smaller clusters in being more likely to gain another ion than to lose one. The rate of production of nuclei was described by

$$\mathrm{d}[X_p]/\mathrm{d}t = km_i^p,$$

it being assumed that nucleation did not effectively change the initial concentration, m_i. k and p are constants, the latter being the number of ions required to form the critical nucleus. Precipitation was observed when a constant fraction of the solute had been deposited and the length of the well-defined induction period, t, was given by

$$k = tm_i^{(p-1)} \tag{7}$$

The "constant number" theory of Christiansen and Nielsen differs from the classical theories outlined above in that the latter predict a nucleus size and nucleation rate markedly dependent on the supersaturation. In the former, on the other hand, the nucleation rate is much less dependent upon supersaturation, and the size of the nucleus is constant. The two views have been reconciled to some extent by Collins[22] who treated the non-steady-state problem of nucleation by a method analogous to that involved in heat conduction. He obtained a lower limit for the time required to build up a steady-state concentration of embryos which was independent of the free-energy of formation of the critical nucleus.

Recently, Lothe and Pound[23] have reconsidered the classical nucleation theory in the light of the quantum-mechanical contributions to the free-energy of formation of nuclei, arising from their absolute entropy. The Gibbs free energy of the classical theory [eqn. (4)] does not take into account the free-energy change due to (i) the decrease in entropy accompany-

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[21] Christiansen and Nielsen, *Acta Chem. Scand.*, 1951, **5**, 673.

[22] Collins, *Z. Elektrochem.*, 1955, **59**, 404.

[23] Lothe and Pound, *J. Chem. Phys.*, 1962, **36**, 2080.

ing the separation of nuclei from the bulk phase, (ii) the translational degrees of freedom of the embryo, and (iii) the change in rotational free-energy of formation of an embryo. Although the evaluation of these terms is difficult because of the uncertainty in the values of the partition functions, Lothe and Pound were able to explain the anomalous pre-exponential factor for the homogeneous nucleation of crystals from supercooled mercury which had been observed by Turnbull.[24] This was a factor of 10^7 higher than that predicted by classical theory. In order to make these calculations, Lothe and Pound neglected the vibrational contributions, by assuming that the force of attraction between embryos was negligible, and the translational contributions, since the crystallites have a very small free volume.

Returning to the crystallisation of electrolytes in solution, Christiansen and Nielsen,[21] using a very rapid mixing obtained by a flow technique, were able to measure the times, t, for visible precipitation extending over a time scale of 10^4—10^6. For silver chromate and barium sulphate, linear plots of log t against log (salt concentration) were obtained and the application of eqn. (7) enabled the evaluation of p, the number of ions in the critical nucleus. The results of these and similar experiments were summarised by Nielsen[25] who showed that silver chloride, calcium oxalate, calcium fluoride, and potassium perchlorate behaved similarly (Fig. 1). Estimated values of p were: 8 for barium sulphate, 6 for silver chromate, and 9 for calcium fluoride, corresponding to equivalent molecular units of 4, 2, and 3, respectively. This approach to the problem of critical nucleus size is very useful but it is essential to deal with situations in which the nucleation is strictly homogeneous. When supersaturation is produced by the rapid

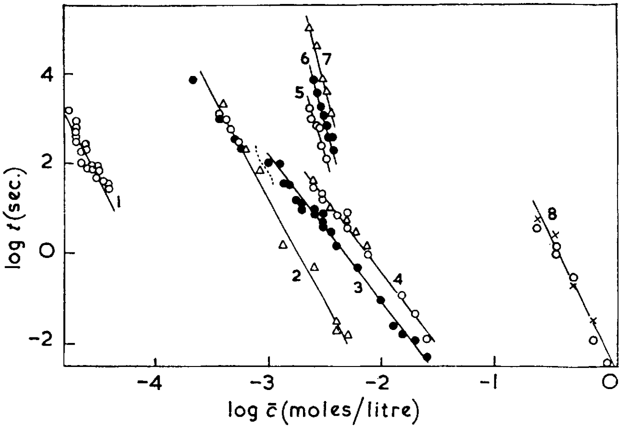

FIG. 1. *Plots of log (induction period) against log (salt concentration).* Curve 1, AgCl 2, Ag_2CrO_4; 3 and 4, CaC_2O_4; 5, 6, and 7, CaF_2; 8, $KClO_4$. (reproduced, by permission, from *J. Colloid Sci.*, 1955, **10**, 576).

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[24] Turnbull, *J. Chem. Phys.*, 1952, **20**, 411.

[25] Nielsen, *J. Colloid Sci.*, 1955, **10**, 576.

mixing of two solutions it is possible that heterogeneous nucleation prevails, nucleation probably occurring in small volume elements where the supersaturation is larger than it is after complete homogenisation.

Critical Supersaturation.—In order to avoid disturbances of local supersaturation, La Mer and Dinegar[26] prepared one of the reactants homogeneously by a chemical reaction. In one such study, sulphate ions were produced, in the presence of barium ions, by the reaction of thiosulphate with persulphate:

$$2S_2O_3^{2-} + S_2O_8^{2-} \rightarrow 2SO_4^{2-} + S_4O_6^{2-}$$

and the time of onset of precipitation observed. Under these conditions they found a critical supersaturation ratio of $(K_{cp}/K_{sp})^{\frac{1}{2}}$ which was constant and equal to 21·5 ± 0·4 over the range of $[Ba^{2+}] = 5\text{—}20 \times 10^{-4}$M. K_{cp} was the product of the activities $\{Ba^{2+}\}\{SO^{2}{}_{4}^{-}\}$, and K_{sp} the corresponding solubility value. A ratio of 21·2 was obtained by these workers on extrapolation of induction times to zero in the direct mixing of dilute solutions of barium nitrate and sodium sulphate. Although these supersaturation limits are remarkably constant, it appears that the nucleation was nevertheless heterogeneous rather than homogeneous, since Collins and Leinweber[27] repeated these experiments and found the observed supersaturation ratio at the time of nucleation to be strongly dependent on the purity of the reagents. The course of precipitation was followed both by conductance and light-scattering measurements and, under given sets of conditions, the ratio was singularly constant. With repeated recrystallisation of reagents, and filtration of solutions, a maximum supersaturation ratio of 32 was reached in water. Any intermediate critical supersaturation could be obtained, depending upon the extent of purification of the reagents. A number of workers, studying the precipitation of barium sulphate by direct mixing of solutions of barium chloride and sulphuric acid have also found varying critical supersaturation limits. The final size of the precipitated barium sulphate was dependent upon the purity of the barium chloride and the age of the reagent solutions.[28,29] Cobbett and French[30] found that barium sulphate would not precipitate below $K_{cp} = 1{\cdot}59 \times 10^{-8}$M^2, whereas La Mer and Dinegar[26] measured an induction period of only 12 min. at this concentration. It is clear that the effect of impurities may explain some of these conflicting results.

Much work has also been done on the nucleation of another analytically important electrolyte, silver chloride. Davies and Jones[11] slowly mixed very dilute solutions of silver nitrate and potassium chloride in a conductivity cell and, using a sensitive a.c. Wheatstone bridge, observed the change in conductivity with time. Extrapolation of the average rate

[26] La Mer and Dinegar, *J. Amer. Chem. Soc.*, 1951, **73**, 380.

[27] Collins and Leinweber, *J. Phys. Chem.*, 1956, **60**, 389.

[28] Bogan and Moyer, *Analyt. Chem.*, 1956, **28**, 473.

[29] Benedetti-Pichler, *Analyt. Chem.*, 1955, **27**, 1505.

[30] Cobbett and French, *Discuss. Faraday Soc.*, 1954, **18**, 113.

of fall of conductivity for very slow precipitations over the first hour or two after mixing gave a critical concentration product $K_{cp} = 2{\cdot}18 \times 10^{-10}\text{M}^2$ when Ag^+ and Cl^- ions were present in equivalent concentrations. Supersaturated solutions having concentration products below this limit showed no tendency to crystallise provided they were prepared by mixing very dilute reactant solutions in order to avoid local concentration effects. It is interesting to note that Kobayashi[31] obtained an induction period of only about 25 min. at this concentration. Davies and Jones[11] found that the value of the critical supersaturation was markedly dependent on the ratio of the silver and chloride ionic concentrations, but not on which ion was in excess. As soon as the product was just exceeded, precipitation took place, although in some cases it was so slow as to be perceptible only after several hours. Klein, Gordon, and Walnut[32] studied the nucleation of silver chloride under "homogeneous" conditions, generating chloride ion by the hydrolysis of allyl chloride. Their critical concentration product, $5{\cdot}48 \times 10^{-10}\text{M}^2$, was appreciably higher than that of Davies and Jones and apparently independent of the ionic ratio. Filtration of the reactant solutions had the unusual effect of lowering K_{cp} and it was suggested that the deionising column used to prepare the water introduced some impurity which inhibited nucleation. No such uncertainty was introduced in Davies and Jones's work since the water was purified by distillation in a Bourdillon still.[11]

Spontaneous Precipitation.—Davies and Jones[11] found the rate of precipitation of silver chloride to be profoundly dependent, for a given initial concentration product, upon the relative concentrations of the solutions being mixed; as shown in Fig. 2. Initiation of crystallisation by the slow addition to the conductivity cell containing silver nitrate of 2 ml. of $4 \times 10^{-3}\text{M}$-potassium chloride produced an initial rate (curve 1) more than 100 times greater than when 20 ml. of a $4 \times 10^{-4}\text{M}$-solution were used (curve 3). Turnbull,[20] rather surprisingly, observed the opposite effect with barium sulphate in that a slower rate of precipitation was obtained on the addition of a relatively concentrated barium chloride solution to a dilute sodium sulphate solution, and concluded that the volume of the added solution was as important as its concentration. He presented his data as a series of curves [Fig. 3(a)] showing the relation between E, the fraction of barium sulphate precipitated [$= (m_i\text{-}m)/(m_i\text{-}m_0)$] and the time, t. By multiplying the time scale by a suitable factor, f, the composite curves were superimposable [Fig. 3(b)], though f varied greatly with the supersaturation ratio, method of mixing, and for different reagent solutions. The overall shape of the $E = F(ft)$ curve was not simple but, since it was observed in all experiments with $0 \leqslant E \leqslant 0{\cdot}40$, Turnbull assumed that the number of precipitation nuclei formed after homogenisation of the solution was negligible in comparison with the number produced during the mixing

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[31] Kobayashi, *J. Chem. Soc. Japan*, 1949, **70**, 125.

[32] Klein, Gordon and Walnut, *Talanta*, 1959, **3**, 187.

process. The dependence of E on (ft) was thus determined by the rate of growth of the particles which were formed during homogenisation.

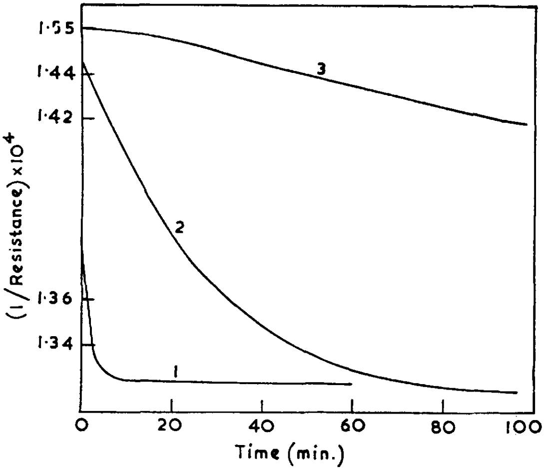

FIG. 2. *Precipitations from unseeded solutions. Plots of (solution resistance)$^{-1}$ against time.*

Addition to $1{\cdot}35 \times 10^{-5}$M-silver nitrate of: curve 1, 2 ml. 0·004M-potassium chloride; curve 2, 10 ml. 0·0008M-potassium chloride; curve 3, 20 ml. 0·0004M-potassium chloride (reproduced, by permission, from *Discuss. Faraday Soc.*, 1949, **5**, 103).

Many other workers also believe that nucleation takes place in the initial process and that it is already negligible before the solution concentration has varied significantly. One method of testing this hypothesis is by observing the number of particles of precipitate formed after mixing the solutions. O'Rourke and Johnson[33] found this to be nearly independent of concentration in the range 2·5—25 × 10^{-4}M when equal volumes of reagents containing equimolar amounts of barium and sulphate ions were

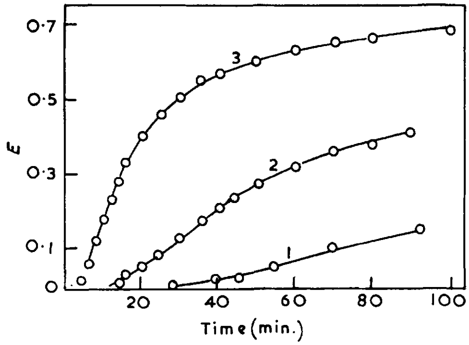

FIG. 3(a). *Plots of E, the fraction of barium sulphate precipitated, against time.*
Curve 1, initial supersaturation, $S_0[=\{Ba^{2+}\}\{SO_4^{2-}\}/K_{sp}^{\frac{1}{2}}]$ = 12·2; 2, S_0 = 15·7; 3, S_0 = 19·0 (reproduced, by permission, from *Acta Metallurgica*, 1953, **1**, 684).

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[33] O'Rourke and Johnson, *Analyt. Chem.*, 1955, **27**, 1699.

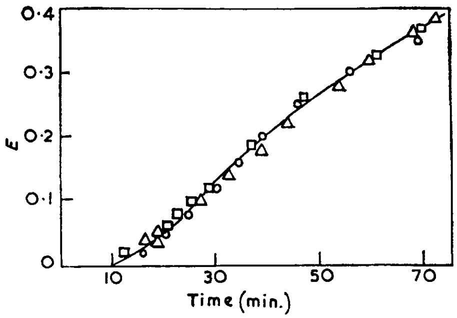

FIG. 3(b). *Superposition of curves shown in Fig.* 3(a). □ $S_0 = 12{\cdot}2, f = 0{\cdot}36$; O $S_0 = 15{\cdot}7; f = 1{\cdot}0$; △ $S_0 = 19{\cdot}0, f = 4{\cdot}1$ (reproduced, by permission, from *Acta Metallurgica*, 1953, **1**, 684).

mixed. This low differential of nucleation rate with respect to concentration led to the conclusion that the extra number of nuclei due to mixing fluctuations was small compared with those formed at a regular rate throughout the observed induction period. The rapid depletion of supersaturation thereafter terminated the nucleation, and precipitation occurred solely through growth. In a similar study with barium sulphate, Nielsen[34] obtained 10^8 particles per litre, which agrees satisfactorily with O'Rourke and Johnson's[33] value of $1{\cdot}2 \times 10^9$. In view of Nielsen's discovery that cleaning of the reaction vessels had a profound effect on the number of particles, it is possible that the constant number observed by O'Rourke and Johnson was due to a fixed concentration of foreign nuclei which offered suitable sites for heterogeneous nucleation. The technique, already described, of slowly increasing the concentration of one of the precipitating ions by a chemical reaction was criticised by O'Rourke and Johnson who considered that the complications arising from a variable nucleation rate created more difficulties of interpretation than did uncertainties due to mixing fluctuations. It is interesting that Davies and Jones[11] found that, after mixing, the precipitation of silver chloride accelerated to a maximum and thereafter the rate curve changed at a fairly well-defined point to a nearly linear rate of decrease (Fig. 4). The turning point was taken as corresponding to the stage at which fresh nuclei ceased to be formed.

A recent study by Fischer[35] in which lead sulphide, cadmium sulphide, and barium sulphate were precipitated from homogeneous solutions, showed that all nucleation occurred in one burst early in the process, within a few thousandths of the total precipitation time. The initial stage of precipitation was shown to be not one of homogeneous nucleation but rather one of direct mixing of the reactant solutions. The number of particles was constant throughout, and the need was again stressed for the careful purification of reagents and preparation of solutions.

All this evidence points to the difficulties inherent in nucleation experi-

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[34] Nielsen, *Acta Chem. Scand.*, 1957, **11**, 1512.

[35] Fischer, *Analyt. Chem.*, 1960, **32**, 1127.

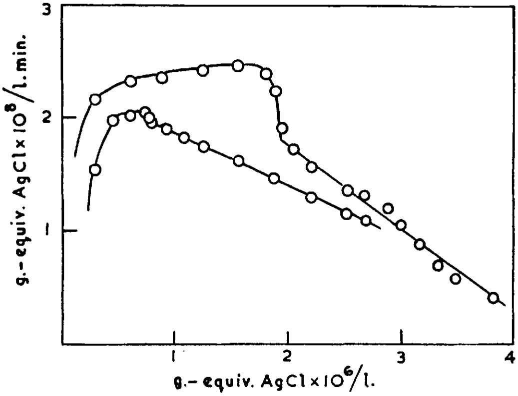

FIG. 4. *Rate of precipitation of silver chloride plotted against amount precipitated in g.-equiv.* × 10^6/*l.* (reproduced, by permission, from *Discuss. Faraday Soc.*, 1949, 5, 103).

ments whether of the direct mixing or "homogeneous" variety. It is very doubtful if any practical medium of precipitation is sufficiently free from available sites to preclude the possibility of induced nucleation. It is impossible to remove completely all impurities from the reagents, and all solutions are in any case in contact with the surfaces of containers. Sites may become detached from a growing crystal and serve as additional centres of growth. For a complete elucidation of the problem it is not sufficient to know only the number of particles formed during precipitation, but entire size spectra of embryos will have to be determined.

Growth

It was Gibbs[36] who first pointed out that growth of perfect crystals must proceed by the formation of a nucleus on the crystal surface and by lateral growth of this monolayer nucleus to the extremities of the crystal face. Thus, energetically, there should be a critical supersaturation below which the crystal would not grow. In 1931, Volmer and Schultze[37] discovered a number of systems in which there was no such critical supersaturation, thus contradicting this theory of growth of perfect crystals. They suggested that there was, at the surface, a mobile self-absorbed layer in thermodynamic equilibrium with the crystal surface. This surface roughness resulted in the possibility of crystal growth without surface nucleation. In a classical work, Frank[38] suggested that the discrepancy observed by Volmer and Schultze had a different origin and that the surfaces of real crystals were imperfect and contained dislocations. A screw dislocation at a crystal surface offered a perpetual growth step and avoided the necessity for

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[36] Gibbs, "Collected Works," Longmanns, London, 1928.
[37] Volmer and Schultze, *Z. phys. Chem.*, 1931, **156a**, 1.
[38] Frank, *Discuss. Faraday Soc.*, 1949, **5**, 48.

two-dimensional nucleation. Following Frank's work there has been a very considerable amount of experimental evidence in its favour. For a large number of substances spiral growth originating at dislocations on the crystal surfaces has been observed. In studies of near-perfect crystals, Sears[6] found that both the Frank mechanism and growth by two-dimensional nucleation may be operative on different planes of a single crystal.

Mechanisms.—Whilst these studies involving the intimate surface structure of the crystals are of great importance, it is possible that kinetic factors might prevail over surface-energy effects, and it is necessary for a full understanding to know something about the mechanism of growth. Measurement of the rate of crystallisation in solution does not give any detailed crystallographic information but it does provide data for comparison with the problems of supercooled liquids and condensation of vapours. Interest in the rates of growth of crystals from solution originated in the question as to whether or not growth and dissolution may be considered to be exactly reciprocal processes.

At its simplest, crystallisation from solution involves (i) the diffusion of solute to the crystal–solution interface, (ii) the adsorption of solute at the surface, (iii) the building of the units into the lattice, and (iv) the opposing process of dissolution. Either crystal growth or dissolution will occur depending upon the relative rates of these steps. It is generally accepted that step (iii) will take place at suitable kinks in the dislocations or molecular terraces on the crystal surface. Apart from this, there is considerable controversy as to whether the reaction is controlled by the diffusion of solute to the crystal surface or whether an interface process prevails. This aspect is of importance because of its direct application to quantitative inorganic analysis, and consequently much of the work has been done on precipitations which involve spontaneous crystallisation.

In the scheme outlined above, if steps (ii) to (iv) were sufficiently rapid to maintain an effective concentration corresponding to saturation at the surface, then (i), the diffusion of material to the surface, would be rate-determining. The flux of solute, in moles sec.$^{-1}$ is given by

$$J_D = Ds\,(m - m_0)/\delta, \qquad (8)$$

where D is the diffusion coefficient, δ the effective thickness of the diffusion layer at the surface, and s the surface area. In reaction-controlled precipitations an analogy may be made to the kinetics of homogeneous solution reactions, the ions being incorporated at growth sites directly from solution. For deposition the flux $J_R = k_n s m^n$ where k_n is the rate constant and n the order of reaction. For dissolution, $J_k = k's$, and in a saturated solution these rates are equal, giving $k' = k_n m_0{}^n$. In a supersaturated solution, assuming that diffusion exerts no influence, the net rate of deposition will be

$$-\mathrm{d}m/\mathrm{d}t = J_R - J_k = k_n s(m^n - m_0{}^n) \qquad (9)$$

However, this equation does not fit the results of growth experiments, and Davies and Jones[11] have pointed out that the analysis of the process into two opposing reactions will not give the correct picture since it is the net change at a fixed reaction site in which we are interested and not just the statistical result of a number of isolated chemical actions.

Experimental Evidence

Spontaneous Growth.—In general, the rate of crystal growth will be a function of two variables, the available surface and the concentration of solute, and at this stage we may write.

$$\mathrm{d}m/\mathrm{d}t = -ks(m - m_0)^n \tag{10}$$

where n is the order of reaction. Many tests of growth equations have been made with experiments involving spontaneous crystallisation. After initial nucleation, the process is treated as one purely of growth, and kinetic interpretations have differed widely. McCabe[39] measured the rate of change of crystal length during growth and for both potassium chloride and copper sulphate found $n = 1$, [eqn. (10)], indicating diffusion control. A close study of the growing-surface of sodium chlorate crystals by Humphreys-Owen[8] and by Amelinckx[40] showed that the concentration of solute was not uniform over any part of a growing-face but was a minimum at the centre, making the concentration gradient highest at this point. The results could again be explained by a formal diffusion theory but it was necessary, in eqn. (10), to substitute for m, a value m', intermediate between m and m_0. First-order kinetics for the growth of $CaSO_4,2H_2O$ from a 175% supersaturated solution were also proposed by Schierholtz[41] although there were marked deviations both at the commencement and termination of the process. In similar studies with barium sulphate, on the other hand, a number of workers have shown that surface rather than diffusion control was indicated with $n > 1$. O'Rourke and Johnson[33] allowed for appreciable changes in surface area during growth, by writing.

$$\mathrm{d}m/\mathrm{d}t = -k\nu^{\frac{1}{3}}(m_\mathrm{i} - m)^{\frac{2}{3}}(m - m_0)^q \tag{11}$$

where ν is the number of crystals per l. They found $q = 4$ for a homodisperse set of growing barium sulphate particles, and $q = 2$ for silver chloride, indicating surface control in both cases. Turnbull[20] has also shown that, for very small barium sulphate particles, surface control was to be expected but as their size increased the growth became diffusion-limited. Nielsen[42] considered that the concentration of the supersaturated solution was important in determining the kinetics. At concentrations above 4×10^{-4}M the crystallisation of barium sulphate was regulated by diffusion of matter from bulk solution to the crystal surface [$q = 1$, eqn. (11)], whilst below

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[39] McCabe, *Ind. Eng. Chem.*, 1929, **21**, 30, 112.
[40] Amelinckx, *J. Chim. phys.*, 1950, **47**, 208.
[41] Schierholtz, *Canad. J. Chem.*, 1958, **36**, 1057.
[42] Nielsen, *Acta Chem. Scand.*, 1958, **12**, 951.

this limit the reaction was interface-controlled, with $q = 4$. From the results of "homogeneous" precipitation experiments, all made above 4×10^{-4}M, diffusion control was again observed.[27]

Seeded Growth.—In all work involving growth from supersaturated solutions following heterogeneous nucleation, it is necessary to make some assumptions about the extent of the nucleation preceding growth. Although it is usually assumed that all nuclei are formed in a short initial period, it is very difficult to determine the instant at which growth predominates. It is possible that, for some time during the precipitation, new nuclei and the growth of existing ones will occur simultaneously. Moreover, it is impossible to reproduce the results of spontaneous crystallisation experiments. Apart from the possibility of heterogeneous nucleation, the movement of the minute new nuclei through the solution may give rise to the enhanced rates of precipitation observed for potassium chlorate by Nielsen.[43] These were attributed to convection around the falling crystals, maintaining a concentration near their surface higher than diffusion alone.

There is little doubt that dissolution of an electrolyte is governed by the rate of diffusion of solute away from the crystal face, and the process follows a first-order equation.[44] The idea of there being strict reciprocity between growth and dissolution was disproved by the classical work of Marc[45] who was the first to demonstrate the inadequacy of the Noyes–Nernst diffusion theory in seeded solutions. Since very small crystallisation velocities were known for supercooled melts, there was no good reason to suppose that they should be much greater in solution. In extensive studies of the rate of growth in seeded supersaturated solutions of a large number of electrolytes, Marc showed that growth differed from dissolution in that (i) it was relatively much slower, (ii) the rate was independent of the rate of stirring if sufficiently vigorous, and (iii) the growth was not necessarily unimolecular. The time relations of the crystallisation velocity were frequently of the second order in his experiments, in which a large quantity of fine crystals were whirled around in the supersaturated solution. In this way, Marc laid the foundations of the adsorption-layer theories of crystal growth, and established the technique of studying the growth of seed crystals. It is well known that the inoculation of supersaturated solutions results in the growth of these added crystals rather than the formation of new nuclei,[46] and the reproducible results obtained in this way enable more reliable tests to be made of growth theories.

Davies and Jones[47] observed the rate of growth of silver chloride seed crystals to be second-order [eqn. (10); $n = 2$], interface-controlled, and independent of stirring rate, and postulated an adsorbed monolayer of hydrated ions at the crystal surface. Formulating the kinetics of crystal-

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[43] Nielsen, *J. Phys. Chem.*, 1961, **65**, 46.
[44] Howard, Nancollas, and Purdie, *Trans. Faraday Soc.*, 1960, **56**, 278.
[45] Marc, *Z. phys. Chem.*, 1908, **61**, 385; 1909, **67**, 470.
[46] Ting and McCabe, *Ind. Eng. Chem.*, 1934, **26**, 1201.
[47] Davies and Jones, *Trans. Faraday Soc.*, 1955, **51**, 812.

lisation in terms of the stationary [Ag^+] and [Cl^-] concentrations in the adsorbed phase, it was assumed that crystallisation occurred through the simultaneous dehydration of pairs of Ag^+ and Cl^- ions. In a non-saturated solution, the hydrated ions left the surface faster than they were replaced by those of the solution, and when equilibrium was reached ions were adsorbed at a rate just sufficient to maintain the monolayer intact. Assuming that every ion striking the surface in a saturated solution entered the adsorbed layer, the rate of adsorption was k_1sm_0 for both the Ag^+ and Cl^- ions. In the case of a supersaturated solution, not all the ions reaching the surface entered the monolayer and the remainder, $k_1s(m - m_0)$ silver ions and a similar number of chloride ions, were available for deposition. These either suffered elastic collisions at the surface of the monolayer or else were incorporated into the crystal lattice when both a Ag^+ and a Cl^- ion arrived simultaneously. The rate of crystallisation for a uni-univalent electrolyte was therefore given by eqn. (10) with $n = 2$. The use of a very sensitive conductance bridge together with well-characterised seed crystals enabled the crystallisation of silver chloride to be followed under conditions in which the change in surface area during an experiment amounted to only 0·1 % of the total surface area of inoculating seed crystals. Eqn. (10), with $n = 2$, was closely followed in solutions in which $r = [Ag^+]/[Cl^-] = 1$ and the reproducibility was also extremely good.[47,48] Similar studies have shown that the same rate expression may be applied to other symmetrical charge-type electrolytes such as magnesium oxalate,[49] barium sulphate,[50] and lead sulphate.[51] In the case of magnesium oxalate, the most soluble of these salts, there was an appreciable amount of a complex, MgC_2O_4, in the supersaturated solution. It was possible to obtain the ionic concentrations [Mg^{2+}] and [$C_2O_4{}^{2-}$] for substitution in eqn. (10) by calculating [MgC_2O_4] from the known value of the association constant. $K = [MgC_2O_4]/[Mg^{2+}][C_2O_4{}^{2-}]f_2{}^2$, f_2 being the activity coefficient of a bivalent ion. The relatively large amount of crystallisation enabled the reaction to be followed by microscopic and titrimetric as well as by conductometric methods. Some typical kinetic plots are shown in Fig. 5.

Any theory of crystal growth must be capable of interpreting the results of experiments in supersaturated solutions containing non-equivalent concentrations of the lattice ions. Eqn. (10), with $n = 2$, applies to cases where $r = 1$ and we can assume that there is no difference of electrical potential between the adsorbed monolayer and the solution. This will not be exactly true since the oppositely charged lattice ions will not be expected to have precisely the same adsorption energies. When their concentrations are non-equivalent, however, it is important to take into account the potential difference ψ between the crystal and the solution. Considering a symmetrical electrolyte, MA, if the cation is in excess, *i.e.*, $[M^{x+}]/[A^{x-}] =$

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[48] Davies and Nancollas, *Trans. Faraday Soc.*, 1955, **51**, 818, 823.
[49] Nancollas and Purdie, *Trans. Faraday Soc.*, 1961, **57**, 2272.
[50] Nancollas and Purdie, *Trans. Faraday Soc.*, 1963, **59**, 735.
[51] Little and Nancollas, unpublished results.

$r > 1$, then the surface will assume a positive potential ψ relative to the solution owing to the adsorption of more cations than anions. The equilibrium value of ψ will be such that equal numbers enter the adsorbed monolayer.[47] An electrical double-layer now surrounds the crystal and the

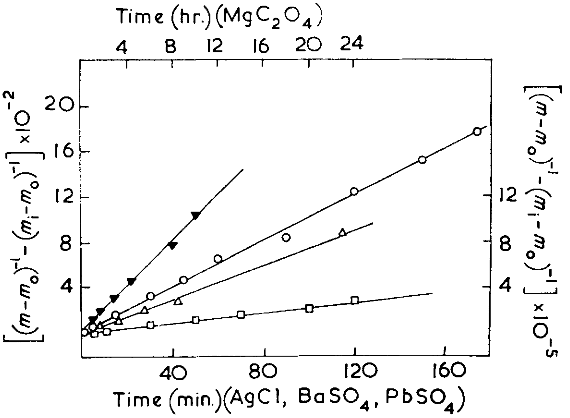

FIG. 5. *Seeded crystallisation from solutions containing equivalent concentrations of lattice ions. Second-order kinetic plots of the integrated form of equation* (10); $[(m - m_0)^{-1} - (m_i - m_0)^{-1}]$ *against time. Left-hand ordinates refer to lead sulphate and magnesium oxalate; right-hand to barium sulphate and silver chloride.* ○, $PbSO_4$; ▲, AgCl; △, MgC_2O_4; □, $BaSO_4$.

availability of M^{x+} ions at the surface $= k_1 s[M^{x+}] \exp(-\psi/\boldsymbol{R}T)$ whilst the availability of A^{x-} ions at the surface $= k_1 s[A^{x-}] \exp(\psi/\boldsymbol{R}T)$ and, since they are equal, $\exp(\psi/\boldsymbol{R}T) = [M^{x+}]^{\frac{1}{2}} [A^{x-}]^{\frac{1}{2}} = r^{\frac{1}{2}}$. The number of ions of each type entering the monolayer in unit time is, as before, m_0, and the rate of crystallisation becomes

$$-\mathrm{d}m/\mathrm{d}t = ks([M^{x+}]r^{-\frac{1}{2}} - m_0)([A^{x-}]r^{\frac{1}{2}} - m_0) =$$
$$ks([M^{x+}]^{\frac{1}{2}}[A^{x-}]^{\frac{1}{2}} - m_0)^2 \qquad (12)$$

This equation has been found to hold very well for the symmetrical electrolytes silver chloride, magnesium oxalate, and barium sulphate, with values of r between 0·25 and 4·0.

Studies with an unsymmetrical electrolyte, silver chromate, indicated that, here also, the same reasoning applied. After an initial induction period which will be discussed later, the growth followed the expression[52]

$$-\mathrm{d}m/\mathrm{d}t = k's\,\{([Ag^+]^2[CrO_4^{2-}])^{\frac{1}{3}} - K_{sp}^{\frac{1}{3}}\}^3$$

reflecting crystallisation through the simultaneous arrival of two Ag^+ ions and one CrO_4^{2-} ion at the surface, enabling the underlying ions to be dehydrated. It was important in these experiments to make allowance for a hydrolysis product $HCrO_4^-$ always present in appreciable amounts in neutral solutions of chromate salts.

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[52] Howard and Nancollas, *Trans. Faraday Soc.*, 1957, **53**, 1449.

On the basis of assumptions very similar to those of Davies and his co-workers, Doremus[53] has suggested two mechanisms by which the ions adsorbed on the crystal surface may combine stoicheiometrically and be incorporated into the crystal lattice. In the first, the adsorbed ions combine to form neutral salt molecules which then diffuse to growth steps. Incorporation of these molecules into the crystal lattice may involve further dehydration of the ions in the surface layer. In order to explain some observed third-order dependencies for 1:1 electrolytes and fourth-order for 2:1 electrolytes in spontaneous growth experiments, Doremus assumed, by analogy with the rôle of a third particle taking part in a gas reaction, that an additional ion stabilised the surface molecule as it was formed, by removing some of the hydration from the combining ions. The rate of formation of the surface molecules was then proportional to $(m - m_0)^3$ for 1:1 and 2:2, and $(m - m_0)^4$ for 2:1 electrolytes. In the second model, the oppositely charged ions are incorporated into the crystal alternatively, directly from the adsorbed layer, at a kink in a growth step. The concentration dependence of the rate of consumption of a solute is then proportional to $(m - m_0)^2$ for 1:1 and 2:2 electrolytes and $(m - m_0)^3$ for 2:1 electrolytes. It is, however, possible to explain these concentration dependencies in terms of the first model only, without the need for the third particle, the rate-determining step being the formation of an ion-pair or neutral molecule in the monolayer. Such was the mechanism proposed by Davies, which has been found to apply to a number of systems. The rate constants, k, will include all factors such as the probability of incorporation of molecules into the crystal lattice and the frequency with which they collide with the growth sites.

Surface Area Considerations.—Although intuitively it is to be expected that the rate of growth of seed crystals would follow linearly their surface area, there is good evidence to indicate that in many systems the effective growth area of the crystals becomes constant at a certain stage in the process even though the crystals increase in size. The second-order rate constants for the growth of magnesium oxalate seed crystals appear to be independent of the appreciable changes in the surface area accompanying the crystallisation.[49] The rate constant is, however, directly proportional to the amount of seed crystals used to inoculate the supersaturated solutions, and it appears that no new growth sites are formed during crystallisation. Doremus[53] has shown that in certain spontaneous crystallisation experiments the effective growth area of the particles may also become constant at a certain point; both barium sulphate and strontium sulphate appear to conform to this behaviour.

Induction Effects in Seeded Systems.—Very many spontaneous crystallisations proceed after an initial induction period, or time lag, during which there is a negligible change in the bulk solute concentration. These

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[53] Doremus, *J. Phys. Chem.*, 1958, **62**, 1068.

are often attributed to the formation of crystal nuclei but such a view must be treated with caution. It is likely that nucleation is completed in a very short time after mixing and, moreover, variations in the duration of the induction period will be due to differences in both the number of nuclei and the growth rate.

Van Hook[12] observed induction periods in the crystallisation of silver chromate when supersaturated solutions were inoculated with seed crystals, which he attributed to a nucleation process. It was shown subsequently, however, that the substantial concentration of the hydrolysis product, $HCrO_4^-$, in the suspensions of seed crystals so affected their surface properties as to produce similar induction effects.[52] Such surface contamination could also be induced artificially by treating seed crystals with adsorbable foreign substances. When used in subsequent crystallisation experiments, induction periods were observed, the durations of which were inversely proportional to the amount of seed suspension used to inoculate the supersaturated solutions.[54] An identical relationship was observed by Van Hook[12] in his experiments with silver chromate.

Even when impurities are absent, induction periods may still be observed. In seeded growth experiments for a given amount of inoculating seed and at the high concentrations obtaining in magnesium oxalate supersaturated solutions, an induction period was observed whenever the initial supersaturation rose above a well-defined value. Its duration was inversely proportional to the supersaturation, and microscopic studies showed that bulk nucleation occurred during the time lag. It is probable that the high concentration gradients tended to build up solute by a diffusion process faster than it could be accommodated on the available growth sites. At supersaturations below the critical value, or when the amount of inoculating seed was increased, the induction period disappeared, enabling second-order growth to set in immediately. The growth of barium sulphate seed crystals[50] may proceed through an initial growth surge, and it is possible that nucleation takes place on the surface of the added crystals during the fast period. The effect could again be eliminated either by providing a sufficient number of growth sites initially or by reducing the supersaturation. The low concentration of the supersaturated solutions compared with those of magnesium oxalate prevented bulk nucleation.

The Effect of Poisons on Crystal Growth.—A process which takes place through the formation of a surface monolayer of hydrated ions would be expected to be profoundly affected by the presence of substances in the solution capable of being adsorbed. The growth of silver chloride seed crystals was retarded by the presence of benzoate, dodecyl sulphate, and cetyltrimethylammonium ions, and was completely stopped in a $4{\cdot}5 \times 10^{-5}$M potassium eosin solution.[48] Phosphates also have a marked effect on

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[54] Davies, Jones and Nancollas, *Trans. Faraday Soc.*, 1955, **51**, 1232.

the growth of lead sulphate[51] and strontium sulphate[55] crystals. The retarding effect of these substances may be explained as being due primarily to the mechanical result of their presence in the adsorption layer. The lattice ions may still be able to deposit, though at a slower rate, when obstructed by adsorbed molecules. As a result, the rate constant is reduced by an amount reflecting the extent of adsorption, and, in the case of silver chloride, a Langmuir adsorption isotherm is followed.[48] As expected, the adsorbates have very little effect on the reverse process of dissolution. Sears[56] discovered that certain complex inorganic ions such as ferric fluoride were effective in retarding both the growth and dissolution of lithium fluoride when present at concentrations of 10^{-5}—10^{-6} molal. He concluded that the poison was adsorbed at growth steps thus reducing the rate of growth, and that the step energy was also decreased. This resulted in a reduction in the critical free energy for two-dimensional nucleation on a perfect surface and an increase in nucleation rate. This was apparently sufficient to lead to a decrease in the overall dissolution rate in the presence of poison.

The influence of poisons upon the specific growth rates of individual crystal faces leads, in many cases, to appreciable habit modification but it is not intended, in the present Review, to discuss the extensive studies in this field.

[55] Otani, *Bull. Chem. Soc. Japan*, 1960, **33**, 1549.

[56] Sears, "Growth and Perfection of Crystals," Wiley, New York, 1958.