CCA-591 541.18.041
Conference Paper

Precipitation

A. E. Nielsen

Medicinsk-Kemisk Institut, University of Copenhagen, Copenhagen, Denmark

A review is given of present knowledge of processes involved in the formation of a crystalline precipitate from a supersaturated liquid solution. Phenomena of homogeneous and heterogeneous nucleation followed by crystal growth on perfect or imperfect crystal faces are discussed. Single mechanism behavior in any step of a sequential reaction chain are exceptions or extreme cases, with most of the real systems showing complex, parallel reaction paths.

Precipitation is the formation of one or more new phases of composition different from that of the original multicomponent single-phased system. In the following we shall in particular consider the formation of a crystalline precipitate from a supersaturated liquid solution, but many of the statements also apply to the formation of droplets or of bubbles[1–9].

The stages of a precipitation process are represented in Fig. 1. Precipitation starts with nucleation on impurity particles (or seeds), or with the formation of embryos. The nuclei grow into visible crystallites. Sometimes the growth process is accompanied by the formation of new (secondary) nuclei[10] so that crystallites of two or more size groups are present. The crystallites may form a stable suspension or they may coagulate. When the crystallites or the coagulated clusters in a liquid become larger they tend to sediment. This is usually the last step of the process, and the growth of the individual particles seems to have ceased. But if the system is observed for a very long time it is evident that the smaller crystallites redissolve and the larger ones grow further. Thermodynamically the system is not stable until all the solute in excess of the amount corresponding to the solubility is united into a single crystal. This is the theoretical termination.

Supersaturation

Precipitation is not possible unless the solution is supersaturated. A saturated solution can be made supersaturated by temperature change or by fractionation through evaporation or crystallization of the solvent. Another way of making a supersaturated solution is to mix two solutions or liquids which react chemically (*e. g.* electrolyte precipitation from aqueous solution) or otherwise (salting out; addition of a poor solvent to a solution in a good solvent).

Nucleation

Precipitation does not start at any supersaturation, no matter how small, because small crystals have a higher equilibrium concentration than large

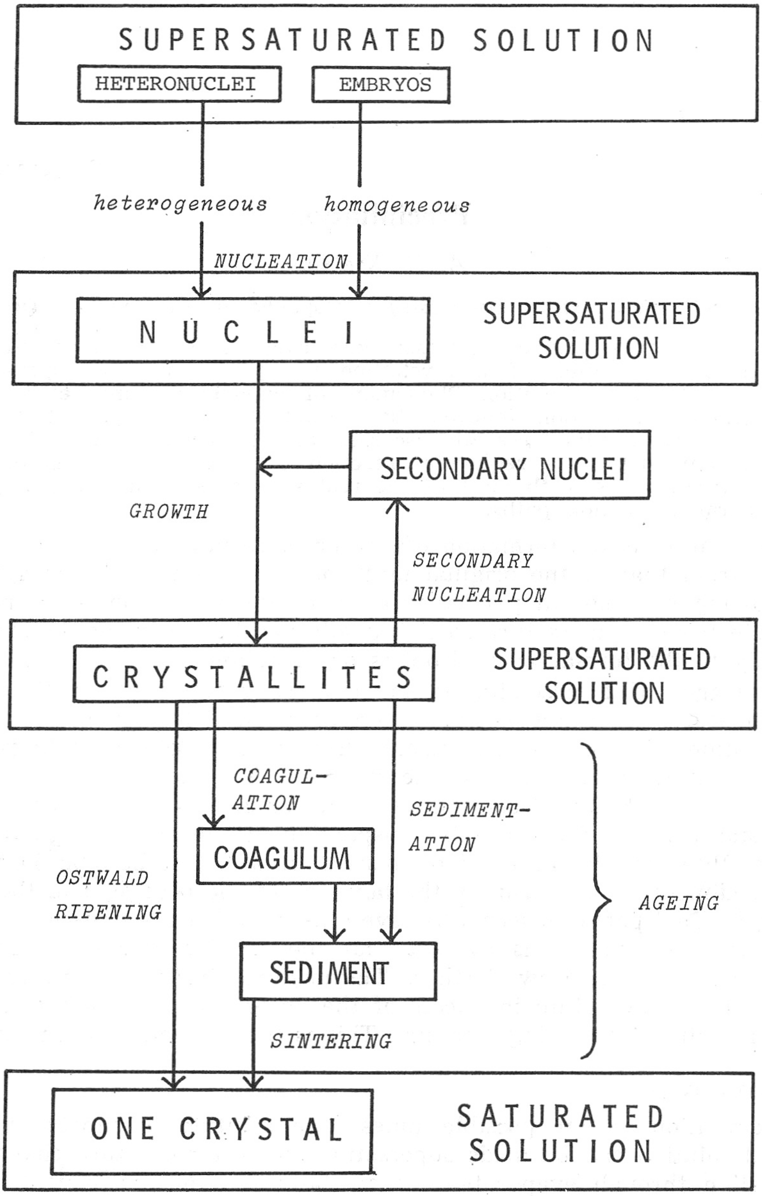


Fig. 1. Ways and stages of precipitation processes.

crystals[11-12]. Although it is almost impossible to measure the interfacial tension between a crystal and a solution, there is no doubt that the interface contributes to the Gibbs free energy of the system, approximately proportional to the area of the interface. If a crystal in a solution is divided into a number of small crystals the interface is increased. If the original crystal was in solubility equilibrium with the solution the small crystals cannot be so. Actually they will begin to dissolve, even at a small finite supersaturation. The smaller a particle is, the higher is the supersaturation required for the particle to be in equilibrium with the solution. This may be demonstrated by blowing bubbles in water by means of straws, or glass capillaries, of different diameters. The narrower the tube is, the smaller are the bubbles, and the harder one has to blow in order to produce the bubbles. It follows that crystals smaller than a certain critical size will dissolve if they are brought into contact with a solution of moderate supersaturation — the critical size depending on the ratio of the concentration to the solubility, whereas crystals larger than the critical size start growing — and grow more and more rapidly, as they get larger (if the solute concentration is kept constant). But we know that crystals often appear from a moderately supersaturated solution. How can that be explained? This can happen in two ways.

Heterogeneous nucleation

Any solution which has not been extremely well cleaned contains a vast number of invisible solid particles. 100 particles per mm^3 is quite normal even in filtered liquids. In fact, it is impossible to remove these particles completely. They may act as heteronuclei, *i. e.* catalysts for the initiation of precipitate crystals, the solute being adsorbed on the particles to form a layer which is larger than a face of a crystal of the critical size, and thus able to grow in the solution. This is the normal way of nucleation of a new phase.

The number of heteronuclei depends on uncontrolled details in the prehistory of the substance used, which makes heterogeneous nucleation a very irreproducible phenomenon[13-14]— although of great practical interest in the chemical industry and because of its influence on the formation of rain, snow, and hail.

Homogeneous nucleation

Even at a moderate supersaturation there is an appreciable number of embryos, *i. e.* subcritical associates of crystal-like structure in equilibrium with the solution, and a small fraction of these reaches the critical size by thermal fluctuation[15-18]. When this happens the chance that the associate will grow further is larger than the chance that it will dissolve again. The critically sized embryos thus play a role similar to the activated complex of chemical reaction kinetics. Homogeneous nucleation has been observed in two types of experiments.

In the first type the growth of the heteronuclei is limited by dividing the system into a very large number of small parts, so that only a small fraction of these contains one or more of the heteronuclei[19-23]. That has been done by forming an emulsion of droplets in another liquid which is immiscible with the solvent. The method has been used in the study of homogeneous nucleation from liquid metals (emulgated in oil). A similar technique is the study of a fog of droplets crystallizing in a carrier gas.

In the other type of experiments a very high supersaturation is produced very rapidly so that the number of homogeneously nucleated particles is much larger than the number of heteronuclei present. This was the method used in the classical work on homogeneous nucleation of vapours of volatile liquids like ethanol and water[24]. It has also been applied to the precipitation of sparingly soluble electrolytes from solution[25-27]. Fig. 2 shows the number of particles formed in a unit volume as a function of the concentration. In case of heterogeneous nucleation the number of particles is roughly constant during the precipitation process, and the particles are of nearly the same size. When homogeneous nucleation takes place the number of crystals increases with time. The rate of nucleation is strongly dependent on the concentration, and approaches zero as soon as the concentration has decreased by a relatively small amount.

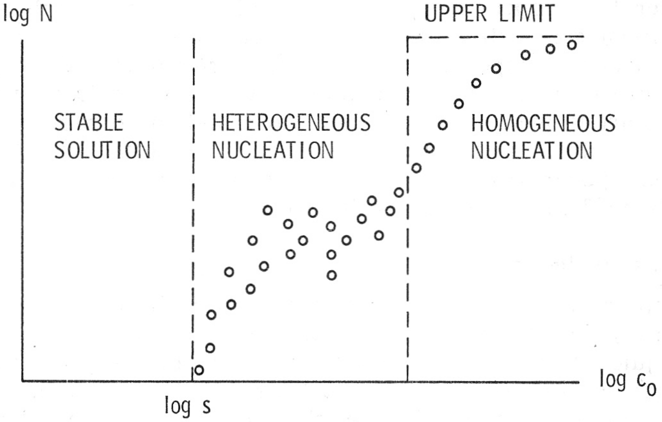


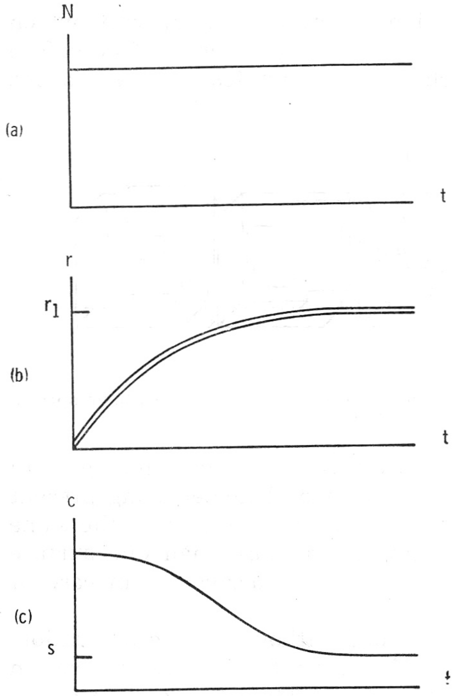
Fig. 2. The number of particles formed in a series of precipitation experiments as a function of the initial concentration. The upper limit is determined by the mixing rate, by coagulation, or by ageing phenomena. N = number of particles formed in a unit volume, c_0 = initial concentration, s = solubility.

Crystal growth

Nucleation in a solution has never been observed directly, because (*a*) the nuclei are extremely small, they often contain less than 100 molecular units (molecules, atoms or ions), (*b*), they are formed at random positions, and (*c*), they are extremely unstable and immediately start to grow. Therefore the nuclei cannot be observed until they have been developed through growth.

Crystals grow by the continued addition of one layer of molecular units on another. The units arrive at the crystal surface by diffusion, sometimes aided by convection, and are fitted to the crystal lattice. The details of adsorption of the units, and of their finding the right place and orientation, are not accurately known.

The rate-determining process may be diffusion through the solution[28], diffusion and convection combined[29], and one or more processes in the crystal-solution interface[1,15-18,30]. As the kinetic equations of diffusion and (laminar) convection are well-known, it is always possible to find out the extent to which a given growth process is controlled by diffusion and convection, if the rate, the crystal size and shape, the concentration, and other relevant parameters are known. However the calculations may be quite complicated[4,29] When a molecular unit has arrived at the crystal-liquid interface it will, in



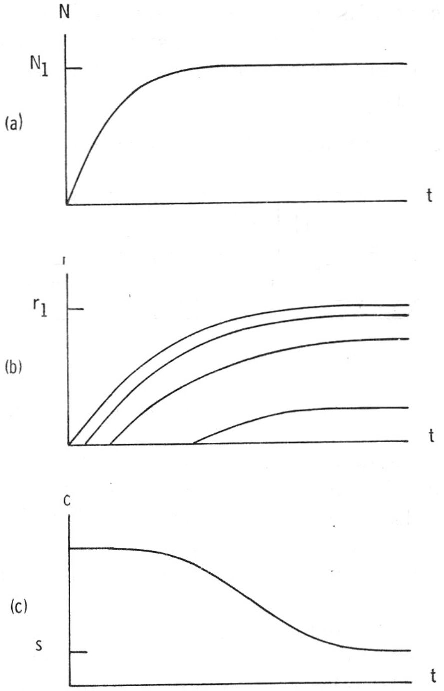


Fig. 3. (*a*) the number N of nuclei in a unit volume; (*b*) the radius r of a crystallite; (*c*) the concentration of the solution, in a heterogeneously nucleated precipitation, plotted as a function of time t.

Fig. 4. The variation of N, r, and c with t in a precipitation with homogeneous nucleation only.

general, be adsorbed, move along the interface and be (partly) desolvated before it enters its future site in the crystal lattice.

Te addition of new layers to the crystal may follow at least four different patterns.

A. Growth on a perfect crystal face

A 1. Mononuclear layer formation (see Fig. 5)

On a perfect crystal face very small surface embroys are unstable and dissolve, but larger surface nuclei grow[1,4,31]. At low degrees of supersaturation

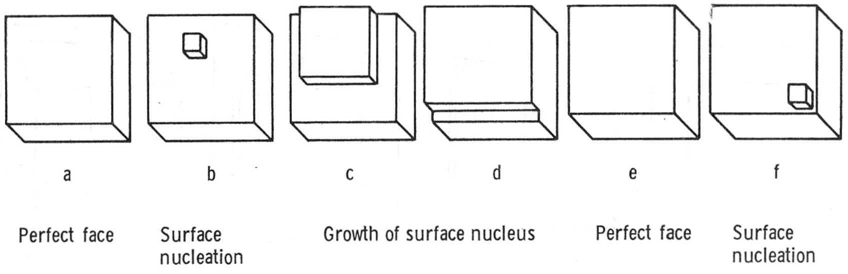


Fig. 5. Series of 'snapshots' of mononuclear growth. The time interval between two surface nucleations is longer than the time it takes a new layer to spread all over the face.

this results in a very slow surface nucleation followed by a growth, which is relativelly slow, but fast enough to spread the layer all over the face before the next surface nucleus is formed. Each layer originates in one surface nucleus.

A 2. Polynuclear layer formation (see Fig. 6)

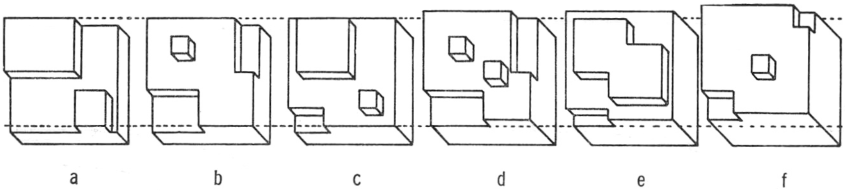


Fig. 6. Polynuclear growth. New surface nuclei are formed before the previous ones have spread. The surface is always covered with nuclei.

Nucleation rates increase more rapidly with concentration than growth rates. At higher concentrations this will result in several nuclei being present at a time on the crystal faces[4,30,31]. The surface nuclei belonging to the same layer grow into each other. Each layer originates in more than one surface nucleus, but the layers in the final crystal are just as perfect as in case of mononuclear layer formation.

On a perfect face no new layer may be formed without surface nucleation, which consequently becomes a bottle-neck for growth. Surface nucleation can only take place when the supersaturation is fairly large (the concentration being many times larger than the solubility. Surface nucleation is mostly observed in controlled laboratory experiments. Most large crystals grow at much smaller supersaturations than those needed for surface nucleation. This is explained by the following mechanism.

B. Growth on an imperfect crystal face

B 1. Spiral step (screw dislocation) growth

Most macroscopic crystals have many lattice defects called dislocations. One type is a screw dislocation. A crystal with a screw dislocation may be visualized (see Fig. 7) as a perfect crystal cut halfway through, distorted and put together again, with an imperfection only visible on two opposite faces, but not on the face from where the cut was made. All the horizontal layers of the crystal shown in Fig. 7 are now parts of one screw layer (or a few

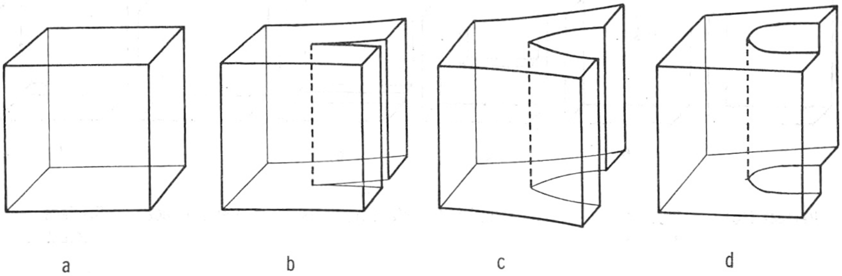


Fig. 7. Drawings illustrating the deformation of the crystal in the vicinity of a screw dislocation.

screw layers if the distortion is larger than the thickness of one layer) winding around the screw dislocation axis shown by broken line in Fig 7. When a crystal has a screw dislocation it can grow without surface nucleation, since the step on the face where the screw dislocation ends will not disappear, however much the crystal grows, and therefore acts as a permanent catalyst for growth, efficient even at very small supersaturations[32–33].

By addition of molecular units the step moves over the crystal surface, and each time it has moved once around the dislocation line the surface has moved by one step high in the direction of its normal. As all parts of the step tend to move with almost the same speed, the step does not move like a hand of a clock (see Fig. 8), but turns into a spiral, with many winds between the dislocation line and the crystal edge — as shown in Fig. 9.

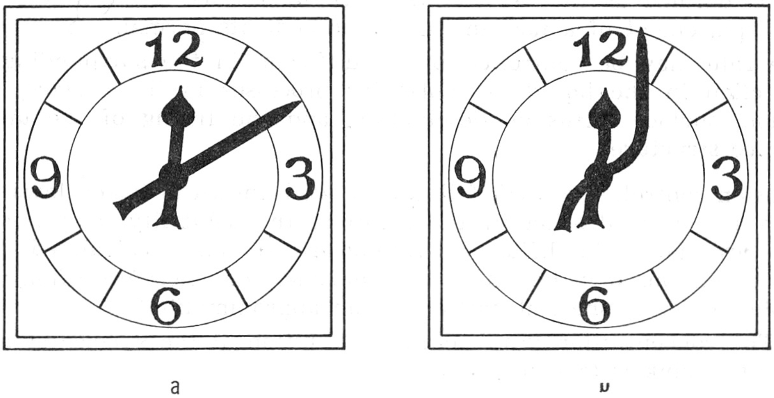


Fig. 8. (*a*) If the step moved like a hand of a clock the outer end of the hand would have to move faster than the inner end. (*b*) If all the points of the hands try to move with the same speed all over, the hands will bend.

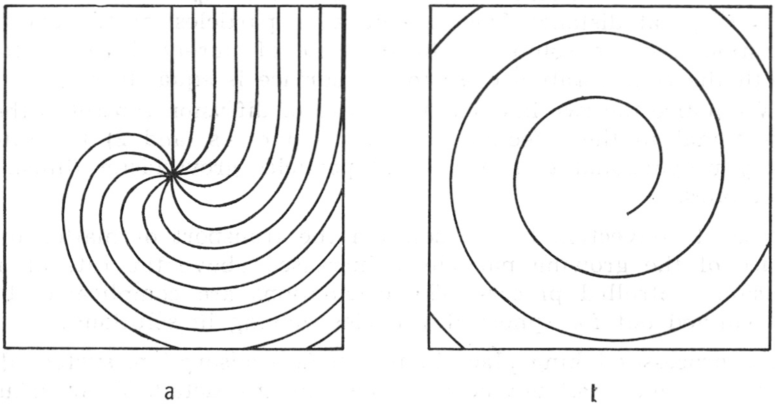


Fig. 9. (*a*) As different parts of the step move at approximately the same speed (except the very innermost part) the step gradually becomes a spiral. (*b*) The resulting spiral.

B. 2. Rough surface

The necessity of nucleation is a consequence of the Gibbs free energy of interfaces. If the interfacial tension is small, nucleation is no longer necessary. In precipitations from solutions of very soluble substances the interfacial tension may become so small that it does not stretch the interface into a plane. Instead the interface becomes molecularly rough. This is often found in metallic systems, but probably never in (*e. g.*) aqueous solutions. When the surface is rough the rate of growth may be very rapid, making heat conduction the rate controlling factor, and macroscopically the surface will follow the isotherm of the equilibrium temperature.

Kinetics of Crystal Growth

Many important conclusions concerning molecular mechanisms of crystal growth can be based on the results of kinetic measurements. The rate of growth is defined as the velocity (relative to a fixed point in the crystal) of the displacement of a face in the direction to its normal.

The rate may be controlled by: 1. diffusion in the surrounding liquid; 2. convection in the liquid; 3. molecular processes in the surface, such as adsorption, surface diffusion, desolvation, and the fitting of the units into the surface structure.

1. Diffusion controlled growth follows the well-known diffusion laws of Fick. When the concentration in the solution, the solubility, and the crystal shape are known the diffusional rate of growth can be calculated, although the calculations may be rather cumbersome. One therefore often uses the simplest case, a spherical particle, as an approximation[34].

   The concentration gradient in the solution at the surface of a sphere acting as sink is (c — s)/r, and

   $$\frac{dr}{dt} = \frac{Dv\,(c - s)}{r} \tag{1}$$

   where dr/dt = the growth velocity; D = the diffusion coefficient; v = the molar volume of the precipitating substance; r = the radius of the spherical particle; c = the concentration of solute in the supersaturated solution, at points of great distance from the growing particles, or the average concentration; s = the solubility. In the case of purely diffusion controlled growth the concentration close to the surface is equal to s.

   We notice the two important features of diffusion control 1) the rate is proportional to the effective concentration c — s, and 2) the rate is inversely proportional to r, *i. e.* small particles grow faster (linearly) than larger ones.

2. In case of convection in the solution the transport of matter up to the surface of the growing particle is increased above the rate of a purely diffusion controlled process. The calculations are complicated, but have been carried out for spherical particles moving in solution[29].

3. Of the processes taking place in the surface adsorption, surface diffusion, and desolvation shall not be mentioned in any detail. Their influence on the absolute rate of growth may be very marked, but can probably be expressed by some more or less constant factor in the rate expression. The

interesting features which enable us to make assumptions about the mechanisms of growth are connected with the influence of the surface structure.

If the crystal surface is perfect, nucleation is necessary for the growth. In case of mononuclear growth each surface nucleus gives rise to a whole layer, and since surface nucleation is a random process the rate is proportional to to the surface area. Nucleation rates are also proportional to a power of the concentration, as the formation of a nucleus containing m molecular units is an m-th order reaction[4]. So we have

$$\frac{dr}{dt} = K_M r^2 \cdot c^m \tag{2}$$

The proportionality between the rate dr/dt and the square of the particle radius r, makes r infinite at a certain finite time. From

$$\frac{dr}{dt} = K \cdot r^2 \tag{3}$$

follows (if $r = r_0$ at $t = t_0$)

$$1/r_0 - 1/r = K (t - t_0) \tag{4}$$

or

$$r = \infty \quad \text{at}\, t = t_0 + 1/Kr_0 \tag{5}$$

Before the radius becomes infinite other mechanisms will take over the rate control, of course, but since the rate changes so strongly with the size this mechanism can explain that some precipitation processes do not seem to start immediately when the supersaturated solution is made, but only after an induction period which may be longer than the period in which the degree of reaction goes from 0.01 to 0.5.

In polynuclear growth the perfect (*i. e.* dislocation free) surface is at all times covered by surface nuclei of different sizes spreading themselves, and intergrowing[30-33]. What happens on a small part of the surface area is independent of the processes elsewhere, and consequently the rate of growth does not depend on the size of the crystal.

$$\frac{dr}{dt} = K_p \cdot c^p \tag{6}$$

It is possible to show[4] that if the spreading rate of the surface nuclei is controlled by local diffusion at their step edges, the »kinetic order«, p, of polynuclear growth is related to the kinetic order of surface nucleation, m, through $3p = m + 2$.

When the growth rate is catalyzed by screw dislocations the surface is covered with the steps of surface spirals (see Fig. 9b)[32-33]. The distance between the steps (consecutive windings of the spiral) is inversely proportional to the effective concentration $c - s$. The velocity of the steps in the direction of a normal to the steps, which is parallel to the crystal face, is also inversely proportional to $c - s$. (Assuming the step velocity to be determined by local diffusion into the step). Therefore the number of steps passing a fixed point on the crystal surface is proportional to $(c - s)^2$. Each time a step passes by a layer of thickness equal to the step height is deposited, and consequently we have the kinetic equation

$$\frac{dr}{dt} = k \cdot (c - s)^2 \tag{7}$$

The diffusion of solute through the solution is only proportional to $c - s$ to the first power. It will therefore become the rate controlling process at high concentrations. Fig. 10. shows the rate and mechanism of growth may change with concentration.

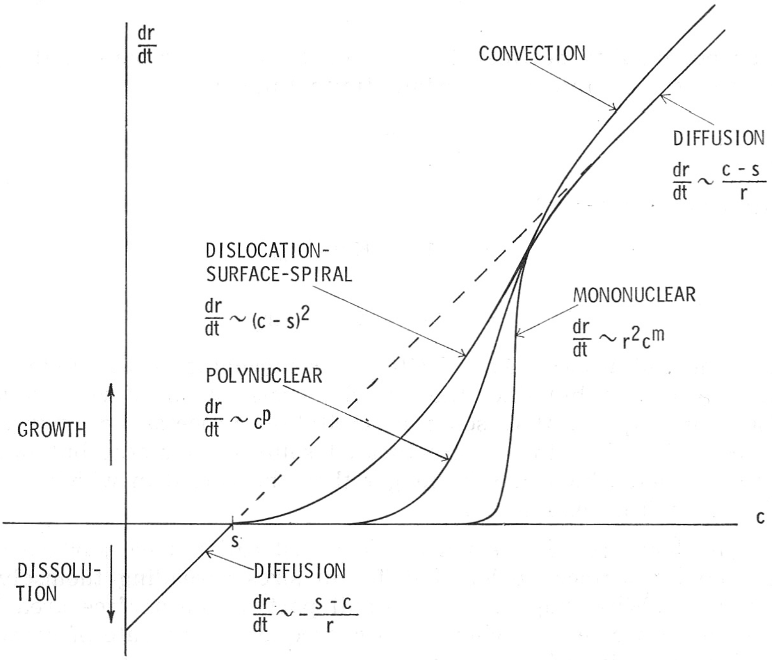


Fig. 10. A schematic diagram showing how the rate and the rate-determining growth mechanism may change with concentration. dr/dt is the linear rate of growth, c = concentration, s = solubility, r = radius or other length dimension of the crystal, m and p are powers on c in the kinetic equations.

Analysis of experiments

In a precipitation experiment one often measures the degree of reaction α as a function of time, where α is defined as the amount precipitated at time, t, divided by the total amount that should precipitate to remove the supersaturation.

The curves start at $\alpha = 0$ at $t = 0$ and converge asymptotically to $\alpha \simeq 1$ when $t \to \infty$.

We assume that the number of particles is constant, originating in heterogeneous nucleation at $t = 0$, and that all particles are alike. It follows that α is proportional to the volume of the particles.

In the first part of a precipitation experiment $c \approx c_0$. Assuming diffusion control we find from equation (1)

$$rdr = Dv\,(c_0 - s)\,dt \tag{8}$$

or

$$r = [2\,Dv\,(c_0 - s)\,t]^{1/2} \sim t^{1/2} \tag{9}$$

As the volume of each particle is proportional both to α and to r^3, we have

$$\alpha \sim r^3 \sim t^{3/2} \tag{10}$$

The rest of the curve $\alpha(t)$ (see D on Fig. 11) can be found by substituting $r = r_1\,\alpha^{1/3}$, $c = c_0 - \alpha\,(c_0 - c)$ into equation (1), and performing the integration[4,35–36].

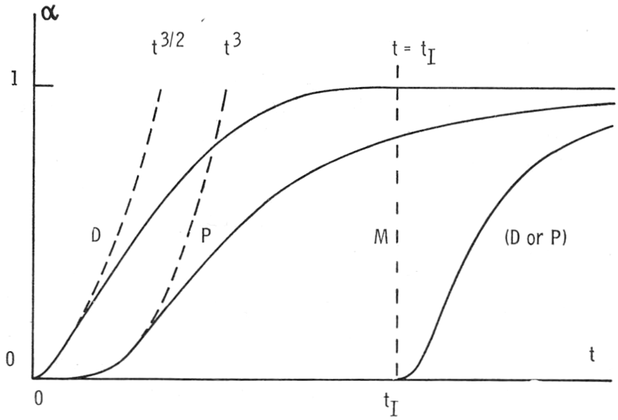


Fig. 11. The degree of reaction, α, (fraction precipitated), as function of time. D = diffusion controlled growth. P = polynuclear growth, M = mononuclear growth. The broken lines are extrapolations of approximate formulae representing the initial stages.

In a precipitation where the rate of growth is independent of the size of the crystals and proportional to the p-th power of the concentration we have, for small values of α,

$$\frac{dr}{dt} = Kc^p \approx K_1 \tag{11}$$

$$r = K_1 t \sim t \tag{12}$$

$$\alpha \sim r^3 \sim t^3 \tag{13}$$

Expressing r and c by means of α and integrating, the theoretical curve may be found[37–39]. See P on Fig. 7.

A mononuclear growth process will be characterized by a period where the presence of the crystals cannot be detected, followed by a period with relatively rapid growth. A plot of $\alpha(t)$ will look like curve M on Fig. 11. The induction period terminates at t_I where continuation of the mononuclear kinetics would lead to infinitely large crystals. After t_I the curve is determined by other factors, such as diffusion control, or a p-th order surface reaction, and may be constructed by parallel displacement of curve D or P in the direction of the t axis. In a plot like Fig. 11 a dislocation controlled process will give a curve of type P with p between 1 and 2.

Compound Mechanisms

In many cases the growth processes are influenced by more than one of the mechanisms described, which correspond to extreme cases. If both diffusion and a p-th order surface reaction influence the rate the slower one among these two will be the most important — it will present a bottle-neck, because the two mechanisms are consecutive. If a polynuclear mechanism and a surface spiral mechanism are competing, the faster one will determine the rate since the two mechanisms operate independently, parallel to each other. The mathematics of compound growth kinetics is somewhat complicated but not intractable[4,40–41].

Suspension stability

Particles in a suspension act on each other by electrostatic and by dispersion forces. If all the particles have appreciable electric charges of the same sign (the sign must be the same if the particles are all alike) they will collide rarely and when colliding, they will probably part again. If the charges are small the particles collide more readily and may stick together because of the short-range dispersion forces, and so the precipitate will coagulate[5,42–49]. Substances which neutralize the charges on the particles — such as »indifferent ions« — may induce coagulation. Other substances which charge the ions electrically — such as specifically adsorbed ions, or ions with a high charge — may stabilize the suspension and thereby prevent coagulation, and may even peptize a coagulated material (redisperse the particles). Some lyophilic colloids which are adsorbed on the particle surface, *e. g.* gelatin, may stabilize a suspension by being adsorbed on the surfaces of the particles, and preventing them from coming so close together that the dispersion forces can keep them together.

Ageing

We have previously noticed that the contribution of the interfacial tension to the Gibbs free energy is proportional to the interfacial area. Therefore the system is not stable until the interfacial area is as small as possible. The decrease of the interfacial area of a precipitate is called ageing. This process takes place through (*a*) recrystallization of the primary particles, transforming *e. g.* needles, thin plates or dendrites into a more compact shape by surface wandering of adsorbed molecular units or by transport through the mother liquid, (*b*) transformation of a crystal from a metastable modification into a stable modification by dissolution and reprecipitation, (*c*) aggregation of primary particles followed by sintering (intergrowth) and (*d*) Ostwald ripening, *i. e.*, growth of the larger particles at the expense of the smaller ones. (*a*) and (*d*) probably always occur in a newly formed precipitate. We shall describe Ostwald ripening in more detail:

We have previously noticed that small particles have a higher Gibbs free energy per molecular unit than larger particles have, because of the larger interface per molecular unit. In other words, the solubility of a small particle is higher than the solubility of a large particle.

If a solution is in contact with three sizes of crystals, and in equilibrium with the middle size, the small crystals will find the solution undersaturated and therefore dissolve, whereas the large particles find it supersaturated — and grow. It follows that a solution cannot be in equilibrium with a precipitate consisting of crystals of two or more sizes[50-55].

If a solution is left with a polydisperse precipitate the concentration will sooner or later reach a value between the solubilities of the largest particles and of the smallest particles, and remain in this interval while the small particles dissolve and the large ones grow, until eventually only one large crystal remains. During the ageing the concentration is close to the equilibrium concentration of a particle with the radius equal to the arithmetic mean value of the radii of all the particles.

Fig. 8 shows how the sizes of a few individual crystals vary during an entire precipitation process, starting with heterogeneous nucleation, followed by homogeneous nucleation, crystal growth, and ageing. When finally the system arrives at the thermodynamically stable ending state, only one single crystal survives.

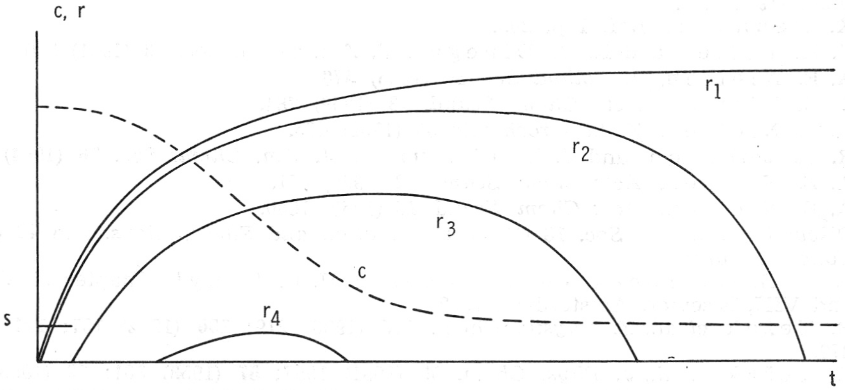


Fig. 12. The concentration (broken line) and the radii of four individual particles (solid lines) as function of time during an entire precipitation process including ageing (Ostwald ripening). All crystals except *one* are eventually redissolved. (Not to scale).

REFERENCES

1. M. Volmer, *Kinetik der Phasenbildung,* Steinkopff, Dresden, 1939.
2. J. Frenkel, *Kinetic Theory of Liquids,* Chapter 7, Oxford U. P., Oxford, 1946.
3. A. Van Hook, *Crystallization, Theory and Practice,* Reinhold, New York, 1961.
4. A. E. Nielsen, *Kinetics of Precipitation,* Pergamon Press, Oxford, 1964.
5. A. G. Walton, *The Formation and Properties of Precipitates,* Interscience Publishers, New York, 1967.
6. R. R. Strickland-Constable, *Kinetics and Mechanism of Crystallization,* Academic Press, London, 1968.
7. R. H. Doremus, *J. Phys. Chem.* **62** (1958) 1068.
8. G. H. Nancollas and N. Purdie, *Quart. Rev.* **18** (1964) 1.
9. A. G. Walton, *Science* **148** (1965) 601.
10. R. F. Strickland-Constable and R. E. A. Mason, *Nature* **197** (1963) 897.
11. W. Thomson, *Proc. Roy. Soc. Edin.* **7** (1870) 63.
12. J. W. Gibbs, (1877) *Scientific Papers,* p. 258 (1906) Yale University Press, New Haven, 1957.

13. E. J. Bogan and H. V. Moyer, *Anal. Chem.* **28** (1956) 473.
14. A. E. Nielsen, *Acta Chem. Scand.* **11** (1957) 1512.
15. M. Volmer and A. Weber, *Z. physik. Chem.* **119** (1926) 277.
16. G. Kossel, *Nachr. Ges. Wiss.*, Göttingen **1927**, 135.
17. R. Kaishew and I. N. Stranski, *Z. Physik. Chem.* **B 26** (1934) 317.
18. R. Becker and W. Döring, *Ann Physik.* **24** (1935) 719.
19. B. Vonnegut, *J. Colloid. Sci.* **3** (1948) 563.
20. D. Turnbull and R. E. Cech, *J. Appl. Phys.* **21** (1950) 804.
21. H. J. De Nordwall and L. A. K. Staveley, *J. Chem. Soc.* **1954**, 224
22. E. R. Buckle and A. R. Ubbelohde, *Pure Appl. Chem.* **2** (1961) 263.
23. E. R. Buckle, *Nature* **186** (1960) 875.
24. M. Volmer and H. Flood, *Z. Physik. Chem.* **A 170** (1934) 273.
25. A. E. Nielsen, *Acta Chem. Scand.* **15** (1961) 441.
26. A. E. Nielsen, *J. Phys. Chem. Solids*, Supplement I, *Crystal Growth,* (1967) 419.
27. A. E. Nielsen, *Kristall und Technik* **4** (1969) 17.
28. W. Nernst, *Z. Physik. Chem.* **47** (1904) 52.
29. A. E. Nielsen, *J. Phys. Chem.* **65** (1961) 46.
30. W. K. Burton and N. Cabrera, *Discussion Faraday Soc.* **5** (1949) 33, 40.
31. O. M. Todes, *Problemi Kinetiki i Kataliza,* **7** (1949) 91.
32. F. C. Frank, *Discussion Faraday Soc.* **5** (1949) 48.
33. W. K. Burton, N. Cabrera, and F. C. Frank, *Phil. Trans. Roy. Soc.* **A 243** (1951) 299.
34. K. Neumann, Ref. 1 p. 209.
35. V. K. LaMer and R. H. Dinegar, *J. Am. Chem. Soc.* **73** (1951) 380.
36. A. E. Nielsen, *J. Colloid Sci.* **10** (1955) 576.
37. A. E. Nielsen, *Acta Chem. Scand.* **13** (1959) 784.
38. A. E. Nielsen, *Z. Elektrochemie* **56** (1952) 465.
39. R. A. Johnson and J. D. O'Rourke, *J. Am. Chem. Soc.* **76** (1954) 2124.
40. A. E. Nielsen, *Acta Chem. Scand.* **12** (1958) 951.
41. A. E. Nielsen, *Acta Chem. Scand.* **13** (1959) 1680.
42. *Discussion Faraday Soc.* **18** (1954), *Coagulation and Flocculations,* and **42** (1966), *Colloid Stability.*
43. J. Th. G. Overbeek, *Colloid Science,* Ed. H. R. Kruyt, Chapter II, VI, VII and VIII, Elsevier, Amsterdam, 1952.
44. B. Težak *et al., Z. Physik. Chem.* **175** (1936) 219; **190** (1942) 157; **191** (1942) 270.
45. B. Težak *et al., J. Phys. Chem.* **55** (1951) 1557; **57** (1953) 301; **59** (1955) 769.
46. B. Težak, *et al., Discussion Faraday Soc.* **18** (1954) 63, 194; **42** (1966) 175.
47. B. Težak, *Croat. Chem. Acta* **40** (1968) 63.
48. J. Kratohvil, M. Orhanović, and E. Matijević, *J. Phys. Chem.* **64** (1960) 1216.
49. M. Mirnik, F. Flajšman, and B. Težak, *Kolloid-Z.* **185** (1962) 138.
50. O. M. Todes, *Zh. fiz. khim.* **20** (1946) 629.
51. O. M. Todes, and V. V. Khrushchev, *Zh. fiz. khim.* **21** (1947). 301.
52. I. M. Lifshitz and V. V. Slyozov, *Phys. Chem. Solids* **19** (1961) 35.
53. C. Wagner, *Z. Elektrochemie* **65** (1961) 581.
54. E. Klein and Moisar, *Ber. Bunsenges. physik. Chemie* **67** (1963) 349.
55. M. Kahlweit, *Z. physik. Chem. N.F.* **36** (1963) 292.

IZVOD

Taloženje

A. E. Nielsen

U preglednom obliku opisani su osnovni procesi uključeni u stvaranje kristaliničnog taloga iz prezasićene tekuće otopine. Polazeći od stanja prezasićene otopine, opisani su fenomeni homogene i heterogene nukleacije, rasta kristala na perfektnoj i imperfektnoj plohi, s posebnim osvrtom na proučavanje kinetike. Analizom

eksperimenata pokazano je da jedinstveni sekvencijalni mehanizam predstavlja samo granične slučajeve, jer je većina realnih pojava posljedica složenih mehanizama, konsekutivnih i paralelnih. Pojave stabilizacije i destabilizacije suspenzija, kao i efekti starenja uključuju se u taj niz, koji bi u slučaju konačne termodinamičke ravnoteže morao rezultirati u jednom jedinom monokristalu.

MEDICINSK-KEMISK INSTITUT
UNIVERSITY OF COPENHAGEN
COPENHAGEN, DENMARK