Nucleation Kinetics

VI *. Steady State Treatment of Nucleation and Growth of Crystalline Precipitates

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The irreversible formation of slightly soluble polymers from dissolved monomers is considered. It is assumed that at a certain time t the concentrations of polymers containing n or less monomers are stationary, that the concentration of polymers containing n + 1 monomers is increasing and that polymers containing more than n + 1 monomers do not exist at the time t.

By means of these assumptions and formerly derived expressions for the steady state rate of nucleation and the steady state distribution of monomers on polymers of different size three equations connecting $1-a$ (the fraction of remaining monomers), $\dot{a}$ (the rate of increase of a), s (the rate of nucleation), a (the initial concentration of monomers) and n are derived.

To solve these equations a relation between w_i (the probability pro unit time that a polymer containing i monomers shall capture a further monomer) $1-a$ and i must be known. If it is known, an equation of the form $\psi (a) = t$ can be derived i.e. $\psi (a)$ is the chronometric integral (the chronomal) of the polymerisaton process. By an appropriate choice of the dependence of w_i on i and $1-a$, viz. $w_i = ka^2$ $(1-a)^2 \sqrt{i}$ the calculated chronomal for the precipitation of barium-sulphate can be made to coincide with that derived from recent (conductometric) experiments by Turnbull and by Johnson and O'Rourke. In agreement with earlier results by Nielsen and the author the recent experiments thus show that the nucleus in the precipitation of barium-sulphate contains 4 molecules.

The choice mentioned above is based only on the experimental results.

In a recent paper (V) it was shown that attainment of steady state (stationarity) concerning the critical cluster (X_4 in (V)) must probably be considered as practically instantaneous.

We shall now discuss the further evolution of the system considered in (V). Immediately after the concentration of critical clusters (in our example x_4)

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* The roman numerals of the preceding papers in this series are indicated in references 1—5.
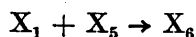
has become stationary the concentration of nuclei (x_5) is of course not stationary, because the reaction

$$X_1 + X_4 \rightarrow X_5$$
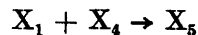
is steadily going on, at first without compensating loss of X_5 either by the reverse reaction

$$X_5 \rightarrow X_1 + X_4$$

or by the capture of a further monomer

$$X_1 + X_5 \rightarrow X_6$$

However, as time goes on x_5 increases and therefore the rates of the compensating reactions will increase. We are asking for the time required for the concentration of nuclei (X_5) to become stationary. We get as before (see V)

$$x_4 w_4 - x_5 w_{-4} = s_4$$
$$x_5 w_5 \qquad\qquad = s_5$$

Multiplication with φ_4 and φ_5, respectively, yields

$$x_4 \varphi_4 w_4 - x_5 \varphi_4 w_{-4} = u_4 \qquad\qquad\text{(a)}$$
$$x_5 \varphi_5 w_5 \qquad\qquad = u_5 \qquad\qquad\text{(b)}$$

Replacing $x_4 \varphi_4 w_4$ by U which is quasi-constant because x_4 has reached its quasistationary value and because $\varphi_4 w_4$ varies very slowly with time and remembering furthermore the relation $\varphi_i w_{-i} = \varphi_{i+1} w_{i+1}$ we get, by addition of (a) and (b), $U = u_4 + u_5$. Omitting differentiation of slowly variable functions we get by differentiation with respect to time from the two equations

$$-\dot{x}_5 \varphi_4 w_{-4} = \dot{u}_4 \qquad\qquad\text{(a)}$$
$$\dot{x}_5 \varphi_5 w_5 = \dot{u}_5 \qquad\qquad\text{(b)}$$

Inserting the obvious relation $-\dot{x}_5 = s_5 - s_4$ in (a) we get

$$s_5 \varphi_4 w_{-4} - u_4 w_{-4} = \dot{u}_4$$

or inserting

$$\varphi_4 w_{-4} = \varphi_5 w_5$$

$$u_5 w_5 - u_4 w_{-4} = \dot{u}_4$$

or

$$U w_5 - u_4 (w_5 + w_{-4}) = \dot{u}_4 \qquad\qquad\text{(c)}$$

whose solution is

$$u_4 = A\, e^{-\lambda t} + U w_5 / \lambda \,; \lambda = w_5 + w_{-4}$$

The constant A may be determined from the condition that at $t = 0$, $x_5 = 0$ and consequently $u_4 = U$. This boundary condition is however of somewhat doubtful validity as it is hard to believe that x_5 is strictly zero when x_4 has become stationary. But the exact value of A is not very important when we consider that the exponential in any case will disappear in a time of the order of magnitude $1/(w_5 + w_{-4})$. According to our assumptions this time is many times larger than the time in which the concentration of critical clusters (X_4) reaches its stationary value, but notwithstanding this it may be small enough

to make the rate s_4 and the concentration x_5 stationary practically instantaneously. In the steady state we get

$$u_4 = Uw_5/(w_5 + w_{-4})$$

or from

$$u_4 = s_4\varphi_4, \quad U = x_4\varphi_4w_4$$
$$s_4 = x_4w_4w_5/(w_5 + w_{-4})$$

or

$$x_4/s_4 = 1/w_4 + w_{-4}/w_4w_5$$

which is the usual steady state value of x_4/s.

We may now treat the next step in a similar way and so on, that is we are lead to the model that at a certain time the concentrations of polymers X_4, $X_5 \ldots X_n$ are stationary while that of X_{n+1} is not and those of higher polymers are zero (at that time).

At a later time the number n has increased but again we may assume that the concentrations of polymers x_i with $i \leq n$ are stationary, while the concentration of x_{n+1} is increasing and higher polymers do not exist at that time.

It is therefore a justifiable program to base the calculation on the assumption of steady state.

THE STEADY STATE TREATMENT

By inspection of the expression arrived at for a reciprocal steady state rate it appears that integration of the rate equation always must lead to an equation of the form: $t = \psi(x)$ where t is the time and x the number of advancement of the overall reaction, that is the number of overall reactions which have taken place in unit volume in the interval from $t = 0$ to t. It is often convenient to replace x by α where α is the degree of advancement of the overall reaction, x and α being connected by the relation $x = a\alpha$ where a is the initial concentration of one of the reactants of the overall reaction.

An integral $\psi(x)$ which actually obeys the condition $t = \psi(x)$ may be called a chronometric integral of the reaction or shorter a chronomal. If somehow a chronometric integral of the reaction in question has been found a great advance in the elucidation of its mechanism has been made.

In the present case the overall reaction is

$$X_1 + nX_1 \rightarrow X_{n+1}$$
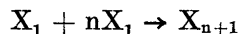
but it is complicated by the fact that n itself increases with time. However we shall see in the following that also in this case it is possible to arrive at an expression of the form $t = \psi(\alpha)$, where α means the fraction of monomers which have formed polymers at the time in question.

As will appear from papers by the author [6-10] (see especially [10] p. 328) we get by the steady state treatment not only information on the form of the rate expression, but also on the distribution of the intermediates. This distribution can be expressed by means of a matrix which may appropriately be called the distribution matrix. To avoid misunderstandings it must be mentioned that the only operations which we shall perform on this matrix are additions either row for row or column for column or both.

Schematically the matrix can be written as follows:

$$
\begin{array}{c|ccccccc}
x_1 & M_{11} & M_{12} & M_{13} & M_{14} & M_{15} & \ldots & M_{1n} \\
x_2 & & M_{22} & M_{23} & M_{24} & M_{25} & \ldots & M_{2n} \\
x_3 & & & M_{33} & M_{34} & M_{35} & \ldots & M_{3n} \\
x_4 & & & & M_{44} & M_{45} & \ldots & M_{4n} \\
x_5 & & & & & M_{55} & \ldots & M_{5n} \\
\cdot & & & & & & & \cdot \\
\cdot & & & & & & & \cdot \\
\cdot & & & & & & & \cdot \\
x_n & & & & & & & M_{nn}
\end{array}
$$

Denoting the sum of each row by M_i this is intended to mean that the concentration of the polymer x_i is proportional to M_i, the proportionality factor being the rate s which is the steady state rate of nucleation. s is not a constant but it is common to the whole system at a given value of n, which is the number of monomers in the largest polymer whose concentration has become stationary at the time in question. It must be emphasized that it has been assumed that there is no backward reaction, that is the solution is strongly supersaturated with respect to polymer X_n. If that were not so the places to the left of the diagonal would not be empty. We can now calculate 1) the concentration x_1 of free monomers and 2) the concentration c_1 of bound monomers, that is the number of monomers bound in nuclei and their descendants at a certain time.

We get:

$$x_1 = sM_1$$
$$c_1 = s \sum_{\nu}^{n} i \, M_i$$

Furthermore we can calculate the total decrease in concentration by application of the following consideration:

Let the flow-sheet below illustrate the situation:

$$(X_1) \rightleftharpoons (X_2) \rightleftharpoons (X_3) \rightleftharpoons \cdots \rightleftharpoons (X_i) \rightleftharpoons \cdots \rightleftharpoons (X_n)$$
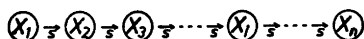
On account of the stationarity the current s is the same everywhere. Therefore the current s_{12} is the same as the current $s_{n,n+1}$ or the number of dimers formed in unit time from $2X_1$ is the same as the number of polymers of degree $n + 1$ formed in unit time from $(n + 1)X_1$. Consequently the decrease in the concentration of monomers must equal $s(n + 1)$. Dividing the equations by a, the initial concentration of monomers, and replacing x_1/a by $1-\alpha$, c_1/a by α and s/a by A we thus get

$$1 - \alpha = M_1 \tag{1}$$

$$\alpha = A \sum_{\nu}^{n} M_i \tag{2}$$

$$\alpha = A(n + 1) \tag{3}$$

Now conforming to our basic assumptions (compare V p. 909) we replace the sum M_1 by its largest term. If the nucleus contains 5 monomers the largest term in M_1 will be of the form $k_1 k_2 k_3 / k_{-1} k_{-2} k_{-3} k_{-4} a^4 (1-\alpha)^4$ that is $M_1 = M_{14}^*$ $= 1/B_1 (1-\alpha)^4$ and generally, if the nucleus contains ν monomers the largest term in M_1 is $M_{1, \nu-1} = 1/B_1 (1-\alpha)^{\nu-1}$. It may be added here that if i denotes the row and j the column inspection of the equations in [10] p. 328 shows that

$$M_{i+1,j} = M_{i,j} w_i / w_-$$

or in our case

$$M_{i+1,j} = M_{i,j} k_i a (1-\alpha) / k_-$$

It will be more important for the following to note that for consecutive columns in the same row

$$M_{i,j+1} = M_{i,j} w_{-j} / w_{j+1}$$

or in our case

$$M_{i,j+1} = M_{i,j} k_{-j} / k_{j+1} a (1-\alpha)$$

We shall now consider the sums M_i beginning with their diagonal terms. In accordance with the general form of the matrix-elements $M_{i,i}$ always equals $1/w_i = 1/k_i a(1-\alpha) = 1/B_i(1-\alpha)$. The next term in the same line becomes $M_{i,i+1} = w_{-i}/w_i w_{i+1}$. From our basic assumption that a nucleus or a crystallite has a much larger tendency to capture a further monomer than to loose one the ratio w_{-i}/w_{i+1} must be small as compared to 1 and the same is true of the following members. Therefore in the case of a non-electrolyte we have good reason to assume that the sum M_i can be represented with sufficient accuracy by its first term $1/B_i(1-\alpha)$. Consecutive diagonal terms are all of this form and may be expected to be of the same order of magnitude.

If the precipitate is formed from ions the situation is a little more complicated. Let us consider for example the case of a slightly soluble binary electrolyte. Let the diagram below represent a part of the flow sheet of the reaction:
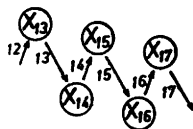
The diagram is intended to show qualitatively the difference in energy between odd and even polymers arising from the electrostatic forces between the ions.

Let us compare at first the diagonal terms of M_{13} (read M thirteen) and M_{14} in the distribution matrix. They are $1/w_{13}$ and $1/w_{14}$. It is evident that w_{13} must be essentially greater than w_{14} because of the electrostatic forces, that is the probability for a say, negatively charged polymer to capture a positively charged monomer must be essentially greater than the probability for a neutral polymer to capture a positively or negatively charged monomer. We therefore consider $1/w_{13}$ to be effectively zero as compared to $1/w_{14}$ and generally in the sum of diagonal terms we may simply omit the odd ones.

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* read M one four

Next we compare qualitatively the significance of the second term in M_{13} and M_{14} respectively. We may write

$$M_{13} = (1 + w_{-13}/w_{14})/w_{13} + \ldots.$$

and

$$M_{14} = (1 + w_{-14}/w_{15})/w_{14} + \ldots.$$

The sum of the two second terms can be written as $(w_{-13}/w_{13} + w_{-14}/w_{15})/w_{14}$. Now the reactions (13) and (15) are of the same type, being reactions between a charged polymer and an oppositely charged monomer. Therefore w_{13} and w_{15} must be expected to be nearly equal. But w_{-13} must be essentially smaller than w_{-14} because the reaction (—13) represents the loss of a charged monomer from a neutral polymer while (—14) represents the loss of a charged monomer from a charged polymer. Therefore the second terms in M_{13} and M_{14} will differ greatly in magnitude and so that the term in M_{13} is essentially less than the term in M_{14}. Application of similar considerations to the higher terms in M_{13} and M_{14} will show that all the terms in M_{13} are essentially smaller than the corresponding terms in M_{14}. We may therefore ignore not only the diagonal terms, but the whole (horizontal) sum corresponding to odd values of i as compared to those corresponding to even values of i.

The second question is whether in M_{14} w_{-14}/w_{15} is essentially greater or less than 1. It is obvious that the ratio w_{-14}/w_{15} is the ratio between the probabilities of two events, loss of a charged monomer from a charged polymer (X_{15}) and capture of a charged monomer by the same polymer (X_{15}), respectively. Without rather problematic assumptions it is, however, not possible to prophecy whether the ratio is greater or less than 1. Experiments on precipitation of barium sulphate, however, seem to indicate that the first alternative is the correct one. We may, however, with some confidence prophecy that the third term in M_{14}, $w_{-14}w_{-15}/w_{14}w_{15}w_{16}$ must be small as compared to the second. The ratio between the third and the second member is w_{-15}/w_{16} which means the ratio between the respective probabilities for loss and capture of charged monomers from the neutral polymer (X_{16}), which is probably small as compared to 1.

From these considerations it appears, therefore, that for a binary salt we may assume

$$M_i = 1/B_i(1-\alpha)^2$$

In the general case, e.g. for a ternary salt we are similarly lead to assume that

$$M_i = 1/B_i(1-\alpha)^\gamma$$

where γ is intergral and greater than zero. In analogy with the case discussed above we shall expect that i for lines whose M_i is not very small is an integral multiple of γ.

Denoting $(1-\alpha)^\gamma B_1$ by P we thus get from (1), (2) and (3) the three equations

$$P = A \tag{I}$$

$$(1-\alpha)^\gamma \alpha = A \sum_{\nu}^{n} i/B_i = AS_n \tag{II}$$

$$\dot{\alpha} = A(n + 1) \tag{III}$$

It will be remembered that B_1 contains the initial concentration of monomers a in the power ν and that similarly the B_i's contain a in the power γ. It will be seen that by the procedure indicated by the equations (1)—(2) and (I)—(II) we have included $x_1, x_2 \ldots x_{\nu-1}$ in the sum which corresponds to 1—a. This is permissible because the sums $M_2 \ldots M_{\nu-1}$ according to our assumptions concerning the nucleation are all very small as compared to M_1. It is also necessary to do so because when we measure, *e.g.* the conductivity of the solution at time zero we cannot avoid to include the small decrease in the concentration of monomers arising from instantaneous nucleation.

It is evident that a knowledge of the dependence of B_i on i is decisive for the solution of the problem. Let us assume that $B_i = i^\sigma \varkappa a^\gamma$, where σ is a fraction. We then get

$$S_n = (\int_\nu^n i^{1-\sigma} di)/\varkappa a^\gamma = (n^{2-\sigma} - \nu^{2-\sigma})/(2-\sigma) \varkappa a^\gamma$$

We may confidently assume that the last term in S_n is disappearingly small as compared to the first. Therefore from equations (II) and (I)

$$\varkappa a^\gamma (1-a)^\gamma a = Q \cdot a = Pn^{2-\sigma}/(2-\sigma)$$

or

$$Q^{1/(2-\sigma)} a^{1/(2-\sigma)} = P^{1/(2-\sigma)} n(1/(2-\sigma))^{1/(2-\sigma)}$$

Using (III) or rather $\dot{a} = P$ n and replacing $1/(2-\sigma)$ by q we get

$$Q^q P^{1-q} a^q = \dot{a} q^q$$

that is

$$\frac{\dot{a}}{a^q Q^q P^{(1-q)}} = q^{-q}$$

As now $Q = \varkappa a^\gamma (1-a)^\gamma$, $P = \beta a^\nu (1-a)^\nu$ where $\varkappa$ and β are constants, integration yields

$$\int_0^a a^{-q}(1-a)^{-p} da = \varkappa^q \beta^{(1-q)} a^p q^{-q} t$$

where $\qquad q = 1/(2-\sigma)$ and $p = \gamma q + \nu(1-q)$

If q and p are known we have thus found the chronometric integral of the polymerisation process.

The weak (or the weakest) point in the derivation seems to be the assumption that the largest term in M_i can be represented by $1/B_i(1-a)^\gamma$ where $B_i = \varkappa a^\gamma i^\sigma$. Actually the author was lead to the assumption of proportionality between B_i and i^σ by a numerical treatment by A. E. Nielsen of Turnbull's very accurate conductometric investigation of the precipitation of barium sulphate. Nielsen found by trials that the degree of conversion a according to Turnbull's result could be accurately represented by the expression

$$\int_0^\gamma a^{-2/3}(1-a)^{-4} da = kt$$

that is q = 2/3, p = 4. That q = 2/3 follows with some certainty from Turnbull's finding, that a when small is proportional to the cube of t. Assuming 1—$a \simeq$ 1 integration yields $a^{1/3}$ = 1/3 kt. That p = 4 came out by trials with other integral values of p. It must be added that Johnsen and O'Rourke [12] on the basis of their own experiments on the same reaction have arrived at exactly the same expression for its chronometric integral. From q = 2/3 follows σ = 1/2, and from p = 4 = γ 2/3 + ν/3 it follows that γ = 2 and ν = 8. For integral values of γ and ν no other values are possible. Attention may be drawn to the fact that Nielsen and the author [2] arrived at the conclusion that ν for barium sulphate was equal to 8. Obviously the expression $B_i = \varkappa a^2 \sqrt{i}$ for a binary electrolyte requires further discussion as it is by no means evident that the expression should be of this form. In the present situation the correctness of the form of the chronomal has therefore only been proved experimentally and that only in one case. The problem is being further attacked in this laboratory from the experimental and from the theoretical side. The outstanding theoretical problem seems at present to be a derivation of the dependency of B_i on i from a definite physical picture.

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