

On Attainment of the Stationary (Steady) State in Nucleation

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The steady state treatment of the nucleation process in precipitation reactions has been supplemented by a treatment which takes the time of attainment of the steady state into account. The results are only valid in a time interval in which the composition of the solution is effectively the original one.

Comparison with experiments from elsewhere indicates that the attainment of the steady rate of nucleation is nearly instantaneous.

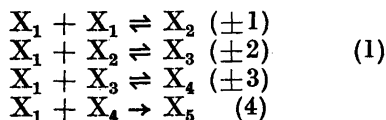
Careful comparison of the author's¹ treatment (1951) of nucleation kinetics with Becker and Dörings'² treatment (1935) shows exact agreement in principle. Both of them are incomplete in so far as only the steady state was considered.

The basic idea in the author's paper was that the nucleation process begins with the successive formation of polymer clusters of increasing size. Polymer clusters have the property of being much more prone to lose a monomer than to capture an additional one.

In contrast to this a nucleus has the property of being much less prone to lose a monomer than to capture an additional one. In the flow sheet (I) below X_4 is the last cluster and X_5 the nucleus. It follows that the further growth of nuclei to visible crystallites is assumed to be effectively irreversible.

We shall now try to complete the treatment of the case of formation of polymers from monomers.

Let the sequence of reactions (1) and the corresponding flow-sheet (I) be



The resulting rates of the reactions (s_i) are

$$\begin{aligned} x_1 w_1 - x_2 w_{-1} &= s_1 \\ x_2 w_2 - x_3 w_{-2} &= s_2 \\ x_3 w_3 - x_4 w_{-3} &= s_3 \\ x_4 w_4 &= s_4 \end{aligned} \quad (2)$$

When this system is solved for x_i we get

$$1 = s_1 \varphi_1 + s_2 \varphi_2 + s_3 \varphi_3 + s_4 \varphi_4 \equiv u_1 + u_2 + u_3 + u_4 \quad (3)$$

$$\varphi_1 = 1/x_1 w_1; \varphi_2 = \varphi_1 w_{-1}/w_2; \varphi_3 = \varphi_2 w_{-2}/w_3; \varphi_4 = \varphi_3 w_{-3}/w_4 \quad (4)$$

In (2) the w_{-i} are constants while the w_{+i} depend on the concentration x_i of the monomer X_i and through this on time. x_i and s_i may depend explicitly on time. We shall assume that during the nucleation x_i is effectively equal to its initial value a . This must be true according to an estimate due to La Mer³ and based on his comprehensive knowledge of the Tyndall effect: For a precipitate to be visible polymers must contain about 10^9 monomers each and there must be about 10^6 such individuals in one cubiccentimetre of the suspension. On the other hand if the initial concentration of the monomer is 0.01 molar it contains about $6 \cdot 10^{18}$ monomers in one cubiccentimetre.

But as a matter of course if the polymers are left to grow by diffusion they will soon collect a major part of the initial monomers, thereby stopping further nucleation. It may be therefore a permissible procedure as an approximation to treat the two phases, nucleation and growth of nuclei, separately although in principle they must evidently result from the integration of one and the same set of differential equations. After this digression we return to our calculations, considering from now on all the w 's and therefore also all the φ 's as constants. Multiplication of the equations (2) with $\varphi_1, \varphi_2 \dots$, respectively, differentiation with respect to time (indicated by a dot) and use of (4) and (5)

$$\begin{aligned} x_1 w_1 \dot{\varphi}_1 &= 1 \\ s_2 - s_1 &= -\dot{x}_2 \\ s_3 - s_2 &= -\dot{x}_3 \\ s_4 - s_3 &= -\dot{x}_4 \end{aligned} \quad (5)$$

finally leads to the following system of equations for the u 's

$$\begin{aligned} u_1 w_{-1} - u_2 w_2 &= -\dot{u}_1 \\ -u_1 w_{-1} + u_2 (w_2 + w_{-2}) - u_3 w_3 &= -\dot{u}_2 \\ -u_2 w_{-2} + u_3 (w_3 + w_{-3}) - u_4 w_4 &= -\dot{u}_3 \\ -u_3 w_{-3} + u_4 w_4 &= -\dot{u}_4 \end{aligned} \quad (6)$$

One set of solutions of this system can readily be found by equating the right hand sides of the system (6) to zero. This yields successively

$$\begin{aligned} u_4 &= u_3 w_{-3}/w_4 \\ u_3 &= u_2 w_{-2}/w_3 \\ u_2 &= u_1 w_{-1}/w_2 \end{aligned}$$

Assuming furthermore that $u_1 = \varphi_1/\varphi$, comparison with (4) shows that

$$u_2 = \varphi_2/\varphi; u_3 = \varphi_3/\varphi; u_4 = \varphi_4/\varphi$$

If therefore $\varphi = \varphi_1 + \varphi_2 + \varphi_3 + \varphi_4$ the set fulfills the condition (3). Next we look for a set of time dependent solutions v_1, v_2, v_3, v_4 which must have the property $v_1 + v_2 + v_3 + v_4 = 0$. To find this set (6) must be solved generally. Obviously (6) contains only three independent equations so that the last one may be replaced by $\Sigma v_i = 0$. The solution can be found by a well known method which of course requires the probabilities w to be known. The exact solution however becomes of a somewhat complicated form. To get an impression of the form of the result we shall make two rather drastic assumptions. The first and maybe the least objectionable one is that w_2, w_3 and w_4 are small enough to be neglected besides w_{-1}, w_{-2} and w_{-3} . This assumption agrees with the basic assumption that clusters are much less prone to capture a new monomer than to loose one. The second assumption is that $w_{-1} = w_{-2} = w_{-3}$. The assumption is most probably true so far as orders of magnitude are concerned. But the exact validity of this assumption is doubtful for the reason that a cluster which contains a greater number of monomers presumably will have a greater probability of loosing a monomer than one which contains a smaller number. However, any definite assumption concerning the relative value of w_{-1}, w_{-2} and w_{-3} will be open to some doubt and we may therefore in a first attempt to solve the problem assume them to be equal. There will be no difficulty in refining the treatment by using other perhaps more natural assumptions.

Putting now $w_{-1} = w_{-2} = w_{-3} = \lambda$ we arrive at the following system of equations:

$$\begin{aligned} \lambda v_1 &= -\dot{v}_1 \\ -\lambda v_1 + \lambda v_2 &= -\dot{v}_2 \\ -\lambda v_2 + \lambda v_3 &= -\dot{v}_3 \end{aligned} \tag{6,1}$$

The boundary conditions are: at $t \rightarrow 0, x_2, x_3$ and x_4 all converge against zero, which by inspection of (2) and the first equation (5) is seen to mean that at $t = 0, u_2 = u_3 = u_4 = 0$.

Successive solution of these equations show that

$$\begin{aligned} v_1 &= \exp(-\lambda t) \\ v_2 &= \lambda t \exp(-\lambda t) \\ v_3 &= 1/2 (\lambda t)^2 \exp(-\lambda t) \\ v_4 &= -(1 + \lambda t + 1/2 (\lambda t)^2) \exp(-\lambda t) \equiv -e_2 \exp(-\lambda t) \equiv -L_2 \end{aligned} \tag{7}$$

form a set of solutions which fulfills the condition $v_1 + v_2 + v_3 + v_4 = 0$. They may be multiplied by any common constant and will still represent a set of solutions with the same property. Adding the values for the stationary case to the time dependent ones we get

$$\begin{aligned} \varphi u_1 &= \varphi_1 + \varphi_4 \exp(-\lambda t) \\ \varphi u_2 &= \varphi_2 + \varphi_4 \lambda t \exp(-\lambda t) \\ \varphi u_3 &= \varphi_3 + \varphi_4 (\lambda t)^2 \exp(-\lambda t) / 2 \\ \varphi u_4 &= \varphi_4 (1 - L_2) \end{aligned} \tag{8}$$

These equations do not exactly conform with the boundary conditions at $t = 0$: $u_1 = 1$; $u_2 = 0$; $u_3 = 0$. The only boundary condition which is exactly fulfilled is $u_4 = 0$ at $t = 0$.

This discrepancy arises from the approximation that w_2 , w_3 and w_4 are disappearingly small as compared to w_{-1} , w_{-2} and w_{-3} : Under this assumption $\varphi \rightarrow \varphi_4$, $\varphi_3/\varphi \rightarrow 0$; $\varphi_2/\varphi \rightarrow 0$; $\varphi_1/\varphi \rightarrow 0$. With these approximations we get in stead of (8)

$$\begin{aligned} u_1 &= \exp(-\lambda t) \\ u_2 &= \lambda t \exp(-\lambda t) \\ u_3 &= (\lambda t)^2 \exp(-\lambda t) / 2 \\ u_4 &= 1 - L_2 \end{aligned} \quad (8,1)$$

which fulfill the boundary conditions.

The only result of these calculations which may be compared with experiments is the expression for $u_4 = s_4 \varphi_4$, where s_4 represents the rate of nucleation \dot{m} . We find

$$\int_0^m \varphi_4 dm = \int_0^t (1 - L_2) dt \equiv y_2 \quad (9)$$

We know from the estimate p. 910 that the precipitate becomes visible before any appreciable alteration of the concentration of monomers has taken place. We therefore treat φ_4 as a constant *i. e.* we write

$$\varphi_4 m = y_2 \quad (9,1)$$

and it must be added, that our system of differential equations (6) has been derived under the said assumption.

The integral y_2 and its first three derivatives are zero at $t \rightarrow 0$. Its fourth derivative at $t \rightarrow 0$ is λ^3 . Let now $w_1 = w_2 = w_3 = w_4 = \varepsilon a$, where a is the initial concentration of X_1 . Using $w_{-1} = w_{-2} = w_{-3} = \lambda$ we thus get

$$m/a = (t \varepsilon a)^4 / 24 \quad (9,2)$$

If t is large as compared to $1/\lambda$, φ_4 still being effectively constant, integration of (9) yields

$$\varphi_4 m = t - 3/\lambda \quad (9,3)$$

that is we find $m \simeq \varepsilon^4 a^5 t / \lambda^3$.

If therefore the precipitate can be observed when m , the concentration of nuclei has reached a certain value, independent of a , we evidently arrive at a relation of the form found experimentally by Tovborg Jensen⁴, Nielsen⁵, La Mer⁶ and other authors.

A more complete discussion requires the integration $\int L_2 dt$ to be performed. Repeated use of partial integration yields $\int_0^0 L_2 dt = 3 - (1 + e_1 + e_2) \exp(-\lambda t)$ which inserted in (9) yields

$$m \lambda \varphi_4 = m \lambda^4 / \varepsilon^4 a^5 = \lambda t - 3 + (1 + e_1 + e_2) \exp(-\lambda t) \quad (9,4)$$

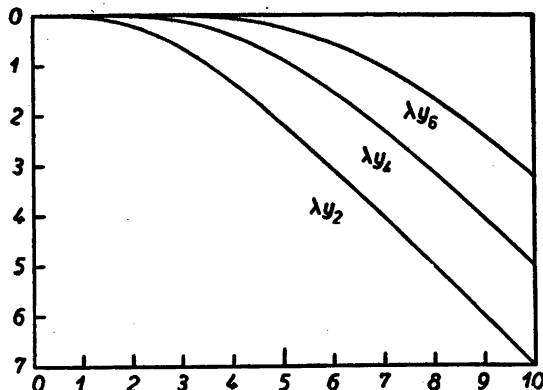


Fig. 1. Graph of the functions λy_2 , λy_4 and λy_6 . For definitions see text. Ordinates and abscissae are pure numbers.

The numerical values of the expression on the right hand side have been calculated for values of λt from zero to ten. Beyond that value the contributions from the last term disappears and the curve thus becomes a straight line. Fig. 1 shows its form. If the power a in (9,4) is greater than 5 the deviation of the curve from its horizontal tangent becomes appreciable at higher values of λt . Curves for

$$\lambda y_4 = \lambda t - 5 + (1 + e_1 + e_2 + e_3 + e_4) \exp(-\lambda t)$$

and

$$\lambda y_6 = \lambda t - 7 + (1 + e_1 + e_2 + e_3 + e_4 + e_5 + e_6) \exp(-\lambda t)$$

are also in Fig. 1.

e_n is defined as

$$e_n = (\lambda t)^n/n! + (\lambda t)^{n-1}/(n-1)! + \dots + \lambda t/1 + 1.$$

If there are n steps in the sequence (2), that is if the nucleus contains $n + 1$ monomers the integral in question becomes y_{n-2} .

DISCUSSION

The calculations above show that the numerical magnitude of λ determines the time of attainment of the stationary (steady) state. If for example $1/\lambda$ is a small fraction of a second the steady state will be reached immediately after the beginning of the process and the experiments by Nielsen⁵ seem to confirm that it is so because, even at precipitation times so small as 10^{-2} — 10^{-3} seconds, an equation of a form analogues to (9,3) without the addend $(n-1)/\lambda$ is fulfilled.

It seems therefore that there is no need to take the time of attainment of the steady state in consideration.

The great problem seems therefore still to be the interplay between nucleation and growth. This has been treated empirically by Tovborg Jensen⁴.

Nielsen and the author⁷ tried to integrate the equations numerically getting only partial agreement with Tovborg Jensens results.

There are also older contributions from Ono⁸, and new experimental material has been procured *inter alia* by Turnbull⁹ and by Johnson and O'Rourke¹⁰. Turnbull's idea is that a number of nuclei are formed at once which then grow by diffusion according to the laws given for the first time by Smoluchowski¹¹ and revised by Frisch and Collins¹². Obviously the difficulties arising from the initial (nucleation) period are avoided by this procedure, but on the other hand it is evident that the results obtained cannot agree with the experiments in the initial period if nucleation is not instantaneous and then stops.

That the number of nuclei which have been formed at a certain not too small time has a limiting value can be seen by numerical integration of the equation

$$\frac{dm}{dt} = Ka^p (1-a)^p$$

where m is the number of nuclei at time t and a is the experimentally determined fraction of monomers which has disappeared from the solution.

It seems therefore to be a sound procedure to do as Johnson and O'Rourke¹⁰ have done, to consider the two phases, nucleation and growth, separately. Anyhow there can hardly be any doubt that in the treatment by Frisch and Collins¹² the assumption $m = \text{constant}$ is fulfilled for the later part of the curves found by Turnbull and others.

In a forthcoming paper, A. E. Nielsen will present some new results and a collection of data from elsewhere.

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