

5-1-1975

## Binary Nucleation. II. Time Lags

Gerald Wilemski

Missouri University of Science and Technology, [wilemski@mst.edu](mailto:wilemski@mst.edu)

Follow this and additional works at: [https://scholarsmine.mst.edu/phys\\_facwork](https://scholarsmine.mst.edu/phys_facwork)



Part of the [Physics Commons](#)

---

### Recommended Citation

G. Wilemski, "Binary Nucleation. II. Time Lags," *Journal of Chemical Physics*, vol. 62, no. 9, pp. 3772-3776, American Institute of Physics (AIP), May 1975.

The definitive version is available at <https://doi.org/10.1063/1.430927>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Physics Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact [scholarsmine@mst.edu](mailto:scholarsmine@mst.edu).

# Binary nucleation. II. Time lags\*

Gerald Wilemski†

Department of Engineering and Applied Science, Yale University, New Haven, Connecticut 06520  
(Received 27 December 1974)

The role of the time lag needed to attain steady state nucleation in binary vapors is discussed. Under appropriate conditions it is possible to obtain both a large predicted rate of binary nucleation and a large time lag. In this circumstance, homogeneous nucleation of the more concentrated component may be the predominant process. It is of obvious importance to the experimentalist to differentiate between these possibilities. Approximate formulas for the time lags are developed, and representative calculations for the ethanol-water system are reported.

## I. INTRODUCTION

In binary nucleation, as in homogeneous nucleation of a single species, the use of steady state theory to calculate rates<sup>1-5</sup> may be invalidated if the time needed to establish the steady state (the time lag) is comparable to the experimental time scale. Moreover, in binary nucleation the time lag might be too large if only one of the two components were present in too small a concentration in the vapor. Then only homogeneous nucleation of the more abundant species would take place, assuming it is supersaturated. Since we envisage experiments in supersonic nozzles and shock tubes with small amounts of condensables present, it is important that reliable estimates of these time lags be made in order to correctly interpret results in terms of either homogeneous nucleation or binary nucleation.

In this paper, approximate formulas for two different time lags needed to establish steady states in binary systems are presented. The present work follows closely that of several predecessors;<sup>6-10</sup> hence, a synopsis of earlier work concerned with homogeneous nucleation will first be presented. The formal results will then be cast into a computationally useful form. The qualitative limiting behavior of the expressions will be discussed, and numerical estimates to time lags in the ethanol-water system will also be presented.

## II. TIME LAG IN HOMOGENEOUS NUCLEATION

One may define a time lag for any time dependent process of interest in the following way. Let  $\alpha(t)$  be a time dependent quantity whose steady state value is  $\alpha_{ss}$ . Next let

$$A(t) = \int_0^t \alpha(t') dt' \quad (2.1)$$

and

$$A_{ss}(t) = \alpha_{ss}(t - \tau) \quad (2.2)$$

The time lag  $\tau$  is the length of time following the initiation of the process ( $t = 0$ ) at which one could fictitiously turn on the steady state value for the process in order that  $A(t)$  and  $A_{ss}(t)$  agree in the limit  $t \rightarrow \infty$ . For example, if  $\alpha(t)$  were the rate of formation of critically sized nuclei, then  $A(t)$  would be the total number of these nuclei formed at time  $t$  after nucleation had begun. The time lag in this case provides a criterion for justifying the use of the steady state rate to calculate the number of critical nuclei formed, as is commonly done. Pro-

vided the time lag is small compared with the experimental time scale, little error is incurred via this procedure. See Andres<sup>6</sup> for more precise remarks about the smallness of the time lag.

Courtney<sup>7</sup> was the first to obtain a formally exact result for the time lag  $\tau_\Gamma$  associated with the rate of formation of clusters of some size  $\Gamma$  larger than the critical size. Andres and Boudart<sup>8</sup> obtained a very general expression for  $\tau_\Gamma$  (among other results) for any linear multistate time dependent process. For the nucleation process they were able to express  $\tau_\Gamma$  solely in terms of steady state and equilibrium quantities. Their result can be expressed as

$$\tau_\Gamma = \sum_{i=2}^{\Gamma-1} (f_i^{ss} - f_i^0) F_i \quad (2.3)$$

where we have the definition

$$\tau_\Gamma = \int_0^\infty dt [1 - I_\Gamma(t)/I_{ss}] \quad (2.4)$$

and

$$F_i = \sum_{j=1}^{i-1} (C_j D_j)^{-1} \quad (2.5)$$

$$f_i^{ss} = C_i (1 - F_i/F_\Gamma) \quad (2.6)$$

$$C_i = C_0 \exp(-\Delta\phi(i)/kT) \quad (2.7)$$

$$D_j = \beta \sigma_j \quad (2.8)$$

In these equations  $I_\Gamma$  is the rate of formation of clusters of size  $\Gamma$ ;  $I_{ss}$  is the steady state value of the rate;  $f_i^{ss}$  is the steady state value of  $f_i(t)$ , the concentration of  $i$ -mers at  $t$ ;  $f_i^0$  is the initial value of  $f_i$ . The equilibrium concentration of clusters is denoted by  $C_i$ , and  $\Delta\phi(i)$  is the free energy of formation of an  $i$ -mer. The quantities  $\sigma_i$  and  $\beta$  are, respectively, the surface area of an  $i$ -mer and the impingement frequency/area of condensible monomer on the cluster surface. Implicit in the derivation of Eq. (2.3) are the following conventions and initial and boundary conditions: The cluster sizes are labeled as  $i = 1$  (monomer),  $i = 2$  (dimer), etc.; the creation of clusters of size  $\Gamma$  is deemed irreversible; and the monomer concentration is held constant:

$$f_1(t) = f_1^{ss} = f_1^0 \quad (2.9)$$

In another article Andres<sup>6</sup> reports some results of Hile<sup>9</sup> regarding other time lags of interest in nucleation. Of particular interest is the time lag  $\tau_n$  for the rate of formation of clusters of size  $n$ , the critical size. This

time lag may be defined as<sup>11</sup>

$$\tau_n = \int_0^\infty [1 - I_n(t)/I_{ss}] dt, \quad (2.10)$$

where  $I_n(t)$  is the net rate of formation of clusters of size  $n$  from size  $n-1$ . Using the results of Andres and Boudart,<sup>8</sup>  $\tau_n$  is given as

$$\tau_n = \tau_\Gamma - F_\Gamma \sum_{i=n}^{\Gamma-1} (f_i^{ss} - f_i^0). \quad (2.11)$$

More recently, Frisch and Carlier<sup>10</sup> have given an independent derivation of  $\tau_\Gamma$ . Their result differs considerably in appearance from Eq. (2.3), but it is easy to show that the two expressions are equivalent. The authors have also considered the problem in which the cluster size is treated as a continuous variable, and they have derived from the differential equation for  $f(t)$  a corresponding expression for  $\tau_\Gamma$ . Of course, this result could be obtained by converting sums to integrals in Eq. (2.3) directly, but in so far as their method is based solely on a partial differential equation for  $f(t)$ , the same techniques can be used advantageously in this paper. This is fortunate because in the theory of binary nucleation recourse is made at the outset to the continuous approximation in order to yield a tractable mathematical problem.

Rearrangement of either Eq. (2.3) or the Frisch-Carlier result for  $\tau_\Gamma$  produces

$$\tau_\Gamma = \sum_{i=1}^{\Gamma-2} (C_i D_i)^{-1} \sum_{j=i+1}^{\Gamma-1} (f_j^{ss} - f_j^0), \quad (2.12)$$

which can be further manipulated to yield

$$\begin{aligned} \tau_\Gamma = & F_\Gamma \sum_{j=n+1}^{\Gamma-1} (f_j^{ss} - f_j^0) + \sum_{i=1}^{n-1} (C_i D_i)^{-1} \sum_{j=i+1}^n (f_j^{ss} - f_j^0) \\ & - \sum_{i=n+1}^{\Gamma-1} (C_i D_i)^{-1} \sum_{j=n+1}^i (f_j^{ss} - f_j^0). \end{aligned} \quad (2.13)$$

With Eq. (2.13), Eq. (2.11) yields

$$\begin{aligned} \tau_n = & \sum_{i=1}^{n-2} (C_i D_i)^{-1} \sum_{j=i+1}^{n-1} (f_j^{ss} - f_j^0) \\ & - \sum_{i=n}^{\Gamma-1} (C_i D_i)^{-1} \sum_{j=n}^i (f_j^{ss} - f_j^0). \end{aligned} \quad (2.14)$$

In the continuous approximation, Eq. (2.12) yields

$$\tau_\Gamma = \int_1^\Gamma du [C(u)D(u)]^{-1} \int_u^\Gamma dg [f^{ss}(g) - f^0(g)]. \quad (2.15)$$

This result can, of course, also be obtained directly from the Frisch-Carlier integral expression for  $\tau_\Gamma$  without resorting to the use of discrete sums. Equation (2.15) can next be written as

$$\tau_\Gamma = T_\Gamma + \tau_n, \quad (2.16)$$

where

$$T_\Gamma = \left( \int_1^\Gamma du [C(u)D(u)]^{-1} \right) \int_n^\Gamma dg [f^{ss}(g) - f^0(g)] \quad (2.17)$$

and

$$\tau_n = \int_1^\Gamma du [C(u)D(u)]^{-1} \int_u^n dg [f^{ss}(g) - f^0(g)]. \quad (2.18)$$

Equation (2.18) can be seen as the continuous approximation of Eq. (2.14).

If the order of integration in Eq. (2.17) is reversed, the dependence of  $T_\Gamma$  on  $\Gamma$  can be readily investigated. With the employment of homogeneous initial conditions, Eq. (2.17) then becomes

$$T_\Gamma = \int_n^\Gamma dx [C(x)D(x)]^{-1} \int_n^x du C(u). \quad (2.19)$$

Let the classical choice for  $\Delta\phi$  in Eq. (2.7) be made

$$\Delta\phi(x)/kT = -\left(x - \frac{3}{2}n^{1/3}x^{2/3}\right) \ln S, \quad (2.20)$$

where  $S$  is the supersaturation. Then the integrand of Eq. (2.19) may be seen to behave as  $[D(x) \ln S]^{-1}$  for large  $x$ . Thus,

$$T_\Gamma \sim \frac{3n}{D(n) \ln S} \left[ \left(\frac{\Gamma}{n}\right)^{1/3} - 1 \right] + \dots \quad (2.21)$$

This expression is clearly of the same order of magnitude as that obtained by Frisch and Carlier<sup>10</sup> for  $\tau_\Gamma$  and also presumably possesses the correct asymptotic dependence on  $\Gamma$ . As previously noted by Andres,<sup>8</sup>  $\tau_n$  is independent of  $\Gamma$  for large  $\Gamma$ . Thus, the partitioning manifested in Eq. (2.16) is appropriate since  $\tau_\Gamma$  is separated into a weakly divergent term,  $T_\Gamma$ , and a finite, constant term  $\tau_n$ , when viewed as a function of  $\Gamma$ .

In the Appendix, the following approximate expression for Eq. (2.18) is derived:

$$\tau_n = \frac{3n}{D(n) \ln S} L(\alpha). \quad (2.22)$$

Values of  $\tau_n$  are listed in Table I and are compared with values calculated using Eq. (2.14). Note the improving agreement as  $n$  increases. This is mathematically consistent with the approximate nature of Eq. (2.18). Also note, as seen in the Appendix, that the integral  $L(\alpha)$  is such a slowly varying function of  $W^*$  (the free energy of critical nucleus formation scaled by  $kT$ ) that it may as well be taken as constant when estimating  $\tau_n$ , particularly when binary systems are involved.

### III. TIME LAG IN BINARY NUCLEATION

#### A. Approximate kinetic equation

Since the partial differential equation for  $f(t)$  now depends on  $t$  and on two composition variables, even in the continuous approximation, the problem of finding a mathematical solution is not such an easy one. However, much progress can be made if we use the same kind of approximation that was used in the steady state analysis.<sup>5</sup> There the steady current streamlines were

TABLE I. Values of the time lag  $\tau_n$  calculated with the exact formula, Eq. (2.14), and the approximate expression, Eq. (2.22). The data of Courtney<sup>7</sup> were used in evaluating these expressions.

$T$ (°K)	$S$	$n$	$\tau_n$ (μsec) (Eq. 2.14)	$\tau_n$ (μsec) (Eq. 2.21)
263.2	5	69	0.41	0.57
233.2	10	43	1.46	2.37
213.2	20	30	3.63	6.98

used to define a curvilinear coordinate system. After transforming coordinates, it was hoped that components of the current vector would be small in the direction perpendicular to the path and could be neglected. This implies that the streamlines are rather smooth paths which change direction only very gradually. The same kind of coordinate transformation could be made for the time dependent problem. However, the introduction of curvilinear coordinates would be purely formal since only in the vicinity of the saddle point is there any knowledge of their form. We will therefore make a simpler coordinate change which, although mathematically exact, is somewhat physically incorrect.

Begin with Reiss' <sup>1</sup> equation for  $f(t)$ :

$$\frac{\partial f}{\partial t} = \frac{\partial I_1}{\partial n_1} - \frac{\partial I_2}{\partial n_2}, \quad (3.1)$$

where

$$I_i = -c(n_1, n_2)\theta(n_1, n_2)\beta_i \frac{\partial}{\partial n_i} (f/c). \quad (3.2)$$

Here,  $n_i$  is the number of molecules of Species  $i$  in the cluster,  $f$  and  $c$  are the nonequilibrium and equilibrium concentrations,  $\theta$  is the surface area of a cluster, and  $\beta_i$  is the impingement frequency/area of Species  $i$  on the cluster surface. The  $I_i$  are the components of the current vector in the coordinate system defined by  $n_1$  and  $n_2$  as the abscissa and ordinate, respectively. Except where otherwise noted, quantities evaluated at the saddle point will be denoted with a superscript \*. Then, with  $\theta$  defined by

$$\tan\theta = n_2^*/n_1^*, \quad (3.3)$$

the coordinate rotation

$$n_1 = s_1 \cos\theta - s_2 \sin\theta, \quad (3.4a)$$

$$n_2 = s_1 \sin\theta + s_2 \cos\theta, \quad (3.4b)$$

produces a coordinate system in which the  $s_1$  axis passes through the saddle point, though in general not along the pass axis which is oriented at a different angle  $\phi$  to the  $n_1$  axis. After transforming coordinates, if the current component in the  $s_2$  direction is assumed to be negligible, Eq. (3.1) may be cast in the form

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial s_1} \left( D(s_1, s_2) c(s_1, s_2) \frac{\partial}{\partial s_1} (f/c) \right), \quad (3.5)$$

where

$$D(s_1, s_2) = \frac{\beta_1 \beta_2 \theta(s_1, s_2)}{\beta_1 \sin^2\theta(s_1, s_2) + \beta_2 \cos^2\theta(s_1, s_2)}. \quad (3.6)$$

Equation (3.5) has the formal appearance of the one dimensional (in composition) equation used in homogeneous nucleation theory and which served as the basis for the work of Frisch and Carlier.<sup>10</sup> Their techniques can then be used with little further qualification. The equation does depend parametrically on  $s_2$ , but only the path  $s_2 = 0$  is being considered. Though this path is not physically the most appropriate, it should be satisfactory because (1) the angles  $\theta$  and  $\phi$  usually differ by no more than a few degrees, and (2) all other quantities are still evaluated at the critical composition and size.

## B. Approximate expressions for time lags

Using the Frisch-Carlier techniques, Eq. (3.5) can serve as the starting point for the derivation of expressions for the time lags of interest. These expressions are formally identical to those in Eqs. (2.17)–(2.19), and there is no need to repeat them. The various quantities appearing in these equations do have some differences, so these are defined below:

$$f^{ss}(s_1) = c(s_1) \int_{s_1}^{\Gamma} dy [c(y)D(y)]^{-1} \times \left( \int_1^{\Gamma} du [c(u)D(u)]^{-1} \right)^{-1}, \quad (3.7)$$

$$D(s_1) = (s_1/s_1^*)^{2/3} D^*, \quad (3.8)$$

$$c(s_1) = c_0 \exp[-w(s_1)/kT], \quad (3.9)$$

$$w(s_1)/kT = -s_1 \ln S(\theta) + (s_1/s_1^*)^{2/3} 4\pi(r^*)^2 \sigma^*/kT, \quad (3.10)$$

$$\ln S(\theta) = \cos\theta \ln S_1(x^*) + \sin\theta \ln S_2(x^*), \quad (3.11)$$

$$S_i(x) = p_i/p_i^*(x), \quad (3.12)$$

$$s_1^* = n_1^* \cos\theta + n_2^* \sin\theta \quad (3.13a)$$

$$= (32\pi/3)(v_1^* \cos\theta + v_2^* \sin\theta)^2 \{\sigma^* [kT \ln S(\theta)]^{-1}\}^3. \quad (3.13b)$$

In these equations,  $r^*$  is the cluster radius,  $v_i^*$  is the partial molecular volume of Species  $i$  in a solution of composition  $x$ , where  $x$  is the mole fraction of Species 2 in the cluster at the saddle point,

$$x = n_2^*/(n_1^* + n_2^*). \quad (3.14)$$

Also,  $p_i$  is the pressure of Species  $i$  in the vapor,  $p_i^*(x)$  is the equilibrium vapor pressure of Species  $i$  over bulk solution of composition  $x$ , and  $\sigma^*$  is the surface tension. Note that for  $s_1 = s_1^*$ , Eq. (3.10) reduces correctly to the form given by Flood<sup>12</sup> and by Mirabel and Katz.<sup>4</sup>

Equations (3.3), (3.6), (3.8), (3.11), and (3.13) along with the results in the Appendix give for  $\tau_n$

$$\tau_n = 3(n_1^* + n_2^*)(D^* \ln S^*)^{-1} L(\alpha), \quad (3.15)$$

where

$$\mathfrak{D}(x) = 4\pi r^{*2} \beta_1 \beta_2 [x^2 \beta_1 + (1-x)^2 \beta_2]^{-1}, \quad (3.16)$$

and

$$\ln S(x) = (1-x) \ln S_1(x) + x \ln S_2(x). \quad (3.17)$$

## C. Limiting behavior of the time lags

Equation (3.15) may easily be used to estimate  $\tau_n$  for different values of the physical parameters involved. Typical values are presented in Table II for the ethanol-water system. Additional insight into the nucleation process in a two-component system may be gained by considering the qualitative behavior of  $\tau_n$  under different limiting conditions.

Consider  $\tau_n$  as a function of the pressures of the different components. Two principal limiting cases occur.

(1) One species is present in low concentration in the vapor. If, for example,  $p_2 \ll p_1$  while a significant percentage of Species 2 was still predicted by thermodynamics to be present in the critical nucleus, then the following limiting form would pertain:

TABLE II. Estimates of the time lag  $\tau_n$  in the ethanol-water system at  $T=273^\circ\text{K}$ . The estimates  $\tau_B$  for binary nucleation were made with Eq. (3.15), and the estimates  $\tau_1$  and  $\tau_2$  for the homogeneous nucleation of water and ethanol, respectively, were made with Eq. (2.22). For these estimates,  $L(\alpha)$  was set at 1.8 for all cases. Listed are the activities of the vapors,  $a_1$  and  $a_2$ , the mole fraction of ethanol in the critical nucleus  $x$ , the time lags, the rate of binary nucleation  $J_B$ , and the rates of homogeneous nucleation of water  $J_1$  and of ethanol  $J_2$ .

$a_1$	$a_2$	$x$	$\tau_B$ ( $\mu\text{sec}$ )	$\tau_1$ ( $\mu\text{sec}$ )	$\tau_2$ ( $\mu\text{sec}$ )	$J_B$ ( $\text{cc-sec}^{-1}$ )	$J_1$ ( $\text{cc-sec}^{-1}$ )	$J_2$ ( $\text{cc-sec}^{-1}$ )
0.1	3.0	0.97	0.17	...	0.17	$1.2 \times 10^{12}$	0.0	$2.0 \times 10^{11}$
1.0	2.33	0.68	0.29	$\infty$	0.37	$1.0 \times 10^{12}$	0.0	$1.5 \times 10^1$
1.5	2.0	0.42	0.51	12.8	0.66	$4.8 \times 10^{12}$	$\approx 0.0$	$9.5 \times 10^{-12}$
1.8	1.26	0.25	0.79	5.1	9.7	$1.0 \times 10^{12}$	$\approx 0.0$	$\approx 0.0$
3.5	0.009	0.08	1.2	0.57	...	$1.0 \times 10^{12}$	$2.1 \times 10^{-8}$	0.0
5.0	0.0001	0.05	20.6	0.24	...	$1.8 \times 10^{12}$	$3.5 \times 10^5$	0.0
5.8	0.00001	0.04	123.0	0.18	...	$1.4 \times 10^{12}$	$7.6 \times 10^8$	0.0

$$\tau_n \approx \beta_2^{-1} 3(n_1^* + n_2^*) [4\pi(r^*)^2 \ln S^*]^{-1} L \quad (3.18)$$

It is apparent that if  $\beta_2$  is too small the time lag necessary for the attainment of the steady state rate of critical nuclei formation could become large. This observation has an important consequence: Homogeneous nucleation of the more abundant component could be the preferentially observed process under these conditions. Even though the steady state rate of mixed cluster formation might be much higher than that of pure cluster formation, the time lag for attainment of that process would be so large as to preclude its realization. The actual nucleation rate of mixed clusters would then probably be much smaller than the steady state value. The time lag for homogeneous nucleation of Species 1 (in this example) would still be relatively small, and the steady state rate for this process would be attained much sooner, thus providing the principal route for nucleation under these conditions. Both processes are taking place simultaneously, but it is their respective rates of relaxation to the steady state which determine their net effectiveness. This situation is different from the limiting case discussed immediately below.

(2) One species is present in *vanishing* low concentration in the vapor. A consistent theory of nucleation in a binary system should reduce correctly to homogeneous nucleation of one component when the other component is made to vanish.<sup>5</sup> Thus, as  $p_2 \rightarrow 0$ , it follows that  $x^* \rightarrow 0$ . The concentration of Species 2 in the critical nucleus vanishes. For small  $x^*$ ,

$$\begin{aligned} \sin\theta &\approx x^* \quad , \\ \cos\theta &\approx 1 \quad . \end{aligned}$$

Then, in the limit, because  $(x^*)^2$  goes to zero faster than  $p_2$ , Eqs. (3.7)–(3.17) all reduce properly to the form required for homogeneous nucleation of Species 1, the remaining species. Thus, if  $p_2$  is made too small, Eq. (3.18) becomes inappropriate, since the nature of the binary system is changing rather dramatically at this point. To wit, it is essentially no longer a two-component system.

Similar considerations will prevail if, for example,  $p_2^*(x) \rightarrow \infty$  ( $x \neq 0$ ). In this case, the free energy of mixing of the two components will be very unfavorable and nearly all pure clusters of Species 1 will form preferentially,

provided Species 1 is in a supersaturated state.

#### IV. CONCLUDING REMARKS

The importance of having reasonable estimates of the time lags of interest should be reemphasized. Even though nucleation theory might predict a high rate of mixed cluster formation in the steady state, this steady state might be kinetically unattainable. In this case, if homogeneous nucleation of one of the components were possible, the associated time lag would undoubtedly be smaller than that for mixed cluster formation. Hence, steady state homogeneous nucleation of one component would predominate *before* the formation of mixed clusters could be ruled out on the basis of steady state theory. This remark has obvious significance in the interpretation of experimental data on binary systems.

#### ACKNOWLEDGMENTS

I want to thank Professor J. L. Katz for suggesting the problem and Professor J. D. Buckmaster for introducing me to asymptotic methods. I must also express my gratitude to Professor P. P. Wegener for his indispensable assistance.

#### APPENDIX: ASYMPTOTIC BEHAVIOR OF $\tau_n$

Equation (2.10) defines  $\tau_n$  for both homogeneous and binary nucleation, and Eq. (2.18) gives the explicit form

$$\tau_n = I \int_1^\Gamma du [C(u)D(u)]^{-1} \int_u^n dx C(x) \int_x^\Gamma dy [C(y)D(y)]^{-1} \quad , \quad (A1)$$

where

$$\Gamma^{-1} = \int_1^\Gamma du [C(u)D(u)]^{-1} \quad . \quad (A2)$$

Of course, for binary nucleation  $n = s^*$ . Employing Eqs. (2.20) and (3.10), Eqs. (2.7) and (3.9) may be written as

$$C(u) = C_0 \exp\{2W^*[(u/n) - (3/2)(u/n)^{2/3}]\} \quad , \quad (A3)$$

where

$$W^* = (1/2)n \ln S \quad (A4)$$

for homogeneous nucleation, and

$$W^* = (1/2)s_1^* \ln S(\theta) \quad (\text{A5})$$

for binary nucleation. For either case,

$$D(u) = (u/n)^{2/3} D^* \quad (\text{A6})$$

and  $D^*$  may be readily determined from either Eq. (2.8) or (3.6).

Now make the successive variable changes:

$$\nu = (u/n)^{1/3}, \quad \omega = (x/n), \quad \xi = (y/n)^{1/3} \quad (\text{A7})$$

Next make the further substitutions

$$-2W^*[\nu^3 - (3/2)\nu^2] = W^* - \gamma^2 \quad (\text{A8a})$$

$$2W^*[\omega - (3/2)\omega^{2/3}] = -W^* + s^2 \quad (\text{A8b})$$

$$-2W^*[\xi^3 - (3/2)\xi^2] = W^* - t^2 \quad (\text{A8c})$$

These variable changes permit Eq. (A1) to be written as

$$\tau_n = 3\lambda n^2 D^{*n-1} \int_{-\alpha}^{\gamma} dr e^{-r^2} \frac{d\nu}{dr} \int_r^0 ds e^{s^2} \frac{d\omega}{ds} \int_s^{\gamma} dt e^{-t^2} \frac{d\xi}{dt} \quad (\text{A9})$$

where

$$\lambda^{-1} = \int_{-\alpha}^{\gamma} dr e^{-r^2} \frac{d\nu}{dr} \quad (\text{A10})$$

$$\alpha = \{W^* + 2W^*[n^{-1} - (3/2)n^{-2/3}]\}^{1/2} \quad (\text{A11})$$

$$\gamma = \{W^* + 2W^*[\Gamma n^{-1} - (3/2)(\Gamma/n)^{2/3}]\}^{1/2} \quad (\text{A12})$$

Equations (A8) are cubic equations that can be solved exactly to give  $\nu$  and  $\omega$  as functions of  $r$  and  $s$ . Additionally,  $\nu$  and  $\omega$  may be expanded as power series, giving

$$\nu(r) = 1 + \nu_1(3)r + \nu_2(3)r^2 + \dots \quad (\text{A13})$$

$$\omega(s) = 1 + \nu_1(1)s + \nu_2(1)s^2 + \dots \quad (\text{A14})$$

The coefficients are found to be

$$\nu_1(m) = m^{-1}(3/W^*)^{1/2} \quad (\text{A15a})$$

$$\nu_2(m) = m^{-2}(1 - 5m/9)[3/(2W^*)] \quad (\text{A15b})$$

$$\nu_3(m) = m^{-3}[5(1 - 5m/9)^2 - (19m^2/27 - 10m/3 + 11/3)](3/(4W^*))^{3/2} \quad (\text{A15c})$$

and so on.

Using Eqs. (A13) and (A14), let us next write Eq. (A9) as

$$\tau_n = 3\lambda n^2 (D^*)^{-1} \nu_1^2(3) \nu_1(1) \int_{-\alpha}^{\gamma} dr e^{-r^2} \rho(r) \int_r^0 ds \sigma(s) \times \left[ e^{-s^2} \int_s^{\gamma} dt e^{-t^2} + \frac{\nu_2(3)}{\nu_1(3)} + \frac{3\nu_3(3)}{2\nu_1(3)} \left( s + e^{s^2} \int_s^{\gamma} dt e^{-t^2} \right) + \dots \right] \quad (\text{A16})$$

where

$$\rho(r) = \nu_1^{-1}(3) \frac{d\nu}{dr} \quad (\text{A17})$$

and

$$\sigma(s) = \nu_1^{-1}(1) \frac{d\omega}{ds} \quad (\text{A18})$$

TABLE III. Values of  $L(\alpha)$ .

$W^*$	$n$	$\alpha$	$L(\alpha)$
19.88	16	3.60	1.37
44.94	30	5.83	1.78
49.51	43	6.30	1.84
55.53	69	6.87	1.91
72.57	81	7.92	2.03
100.6	125	9.49	2.19

For large  $\alpha$  and  $\gamma$ ,  $\lambda$  is independent of  $\alpha$  and  $\gamma$  and Eqs. (A10) and (A13) give

$$\lambda^{-1} = \sqrt{\pi} \nu_1(3) [1 + \nu_3(3) \nu_1^{-1}(3) + \dots] \quad (\text{A19})$$

The remaining integrals must be done numerically, but several considerations help to simplify matters. (1) Since  $\nu$  and  $\omega$  are known exactly as functions of  $r$  and  $s$ ,  $\rho(r)$  and  $\sigma(s)$  may be calculated numerically with high precision. (2) For large  $\gamma$ , the integrals are independent of  $\gamma$ . (3) Numerical calculations show that only the first term of Eq. (A16) contributes significantly to  $\tau_n$ . With the aid of Eqs. (A15) and (A19), Eq. (A16) may now be written to a good approximation as

$$\tau_n = 3n^2 (2D^*W^*)^{-1} L(\alpha) \quad (\text{A20})$$

where

$$L(\alpha) = \int_{-\alpha}^{\gamma} dr e^{-r^2} \rho(r) \int_r^0 ds e^{s^2} \sigma(s) \operatorname{erfc}(s) \quad (\text{A21})$$

and  $\operatorname{erfc}(s)$  is the complementary error function.

The integral  $L(\alpha)$  was evaluated numerically for several values of  $W^*$ . The results, listed in Table III, show  $L(\alpha)$  to be a very slowly varying function of  $W^*$ :  $L(\alpha)$  increases approximately as  $(W^*)^{1/3}$ .

\*The support of the Power Program of the Office of Naval Research is gratefully acknowledged.

†Present address: Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755.

<sup>1</sup>H. Reiss, *J. Chem. Phys.* **18**, 840 (1950).

<sup>2</sup>G. J. Doyle, *J. Chem. Phys.* **35**, 795 (1961).

<sup>3</sup>C. S. Kiang and D. Stauffer, in *Faraday Symposia of the Chemical Society*, No. 7, 26 (1973). D. Stauffer and C. S. Kiang, *Icarus* **21**, 129 (1974), and other references cited therein.

<sup>4</sup>P. Mirabel and J. Katz, *J. Chem. Phys.* **60**, 1138 (1974).

<sup>5</sup>G. Wilemski, *J. Chem. Phys.* **62**, 3763 (1975); preceding article.

<sup>6</sup>R. P. Andres, in *Nucleation*, edited by A. C. Zettlemoyer (Marcel Dekker, New York, 1969), Chap. 2.

<sup>7</sup>W. G. Courtney, *J. Chem. Phys.* **36**, 2009 (1962).

<sup>8</sup>R. P. Andres and M. Boudart, *J. Chem. Phys.* **42**, 2057 (1965).

<sup>9</sup>L. R. Hile, Ph.D. thesis, Princeton University, 1969. As reported in Ref. 6.

<sup>10</sup>H. L. Frisch and C. C. Carlier, *J. Chem. Phys.* **54**, 4326 (1971).

<sup>11</sup>This definition differs slightly from Hile's.<sup>9</sup> Consequently, Eq. (2.11) also differs slightly from the result which can be obtained from Eq. (24) of Ref. 6.

<sup>12</sup>H. Flood, *Z. Phys. Chem. A* **170**, 286 (1934).