THEORETICAL CHEMISTRY INSTITUTE
THE UNIVERSITY OF WISCONSIN

KINETICS OF HOMOGENEOUS NUCLEATION IN MANY COMPONENT SYSTEMS

Joseph O. Hirschfelder

WIS-TCI-510

5 April 1974

MADISON, WISCONSIN

ERRATA

Page 1, line 4, insert between "...on air pollution." and "Our treatment is...." the following:

For example, it is clear from the experimental work of Giauque *et al.*[13] and the theoretical calculations of Heist and Reiss[14] that the free energy of sulfuric acid-water mixtures involve six distinct hydrates and each of these should be considered as a separate component in calculating the rate of nucleation of sulfuric acid-water droplets in polluted air.

Page 5, line 3, replacing sentence "Thus,...composition." with:

Thus, if we look upon the ΔG surface in terms of "hills and valleys", then a "streambed leading to the top of the pass" would correspond to the locus of points $(y_1, 0, \ldots, 0)$.

Page 6, Eq. (9) should read:

$$\sum_j U_{ij} U_{vj} = \delta_{iv} = \sum_j U_{ji} U_{jv} \qquad (9)$$

Page 6, replacing line below Eq. (9) through line above Eq. (11) with:

Thus, $U^{-1}_{ji} = U_{ij}$. Eqs. (7) and (8) can then be combined into the one relation,

$$\sum_{u,v} U^{-1}_{iu}\left(\frac{\partial^2 \Delta G}{\partial n_u \partial n_v}\right)_c U_{vj} = Q_j \delta_{ij} \; .$$

Multiplying this relation by U_{ki}, summing over k, and making use of Eq. (9), we obtain

$$\sum_v \left[\left(\frac{\partial^2 \Delta G}{\partial n_k \partial n_v}\right)_c - Q_j \delta_{kv}\right] U_{vj} = 0 \; . \qquad (10)$$

Thus, the Q_j are the eigenvalues and the U_{vj} are the eigenvectors of the Hermitian matrix $||(\partial^2\Delta G/\partial n_k \partial n_v)_c||$. The specification of the U_{vj} and the Q_j are completed by requiring that Q_1 be negative. The Jacobi method[15] [where the matrix is transformed to diagonal form by a sequence of plane rotations] is probably the most efficient procedure for computing machine calculations since it determines all of the Q_j and U_{vj} simultaneously. Otherwise, one might determine the Q_j as the solution to the secular equation

$$\left|\left(\frac{\partial^2 \Delta G}{\partial n_k \partial n_v}\right)_c - Q_j \delta_{kv}\right| = 0 \; ,$$

and then, for each j, solve Eq. (11) by the familiar method of elimination.

Thus, if one makes a many-dimensional Taylor series expansion in the vicinity of the point $(y_{1c},0,\ldots,0)$, Page 7, insert below Eq. (13) with:

Here $\sum_j N_j$ is an approximation to the concentration of molecules in the mother phase.

Page 9, line above Eq. (20) should read:

approximated by derivatives[16] so that

Page 10, 3rd line from bottom of page to end of page should read:

concentration and is sometimes a poor approximation when the nuclei are formed by very rapid chilling such as occurs when gases are expanded by flow through a nozzle.

Page 15, line below Eq. (39), replace Ref.(5) by Ref. (12).

Page 16, 2 lines after Eq. (44), parentheses should be put around "1" and "12".

Page 16, insert before "Acknowledgements":

Example: Three Components, $q = 3$

One might expect that for the three-component system, it would be convenient to express the U_{ij} in terms of the Eulerian angles (α,β,γ) . Eq. (8) does provide three relations between these three angles. I succeeded in separating the variables so as to get a single transcendental equation for γ . However, this equation was sufficiently complicated that there is no advantage in treating the three-component system as a special case.

Page 18, add the following references after Ref. (12):

13. W. F. Giauque, J. E. Kunzler, and E. W. Hornung, J. Am. Chem. Soc. 78, 5482 (1956).
14. R. H. Heist and H. Reiss, J. Chem. Phys. (submitted Feb. 1974).
15. For a three-component system, the H.P. 65 mini-computer has a pre-programmed magnetic card for getting both the eigenvalues and eigenvectors. For larger systems, see J. H. Wilkinson, The Algebraic Eigenvalue Problem (Clarendon Press, Oxford, 1965), p. 266.
16. Some of the approximations arising from the replacement of the finite differences by derivatives is considered by E. R. Cohen, J. Stat. Phys. 2, 147 (1970).

KINETICS OF HOMOGENEOUS NUCLEATION IN MANY COMPONENT SYSTEMS*

Joseph O. Hirschfelder

Theoretical Chemistry Institute

University of Wisconsin

Madison, Wisconsin 53706

and

Department of Chemistry and Quantum Institute

University of California, Santa Barbara

Santa Barbara, California 93106

ABSTRACT

Reiss's classical treatment of the kinetics of homogeneous nucleation in a system containing two chemical components is extended to many-component systems. The formulation is analogous to the pseudo-stationary state theory of chemical reaction rates with the free energy as a function of the composition of the embryo taking the place of the potential energy as a function of interatomic distances.

The present treatment is a generalization to many components of Howard Reiss's classical treatment of the kinetics of homogeneous nucleation in a binary system.[1] This generalization is needed in connection with research on air pollution. Our treatment is restricted to the formation of critical nuclei by the addition of one molecule at a time. If some particular clusters are relatively stable and occur in sufficient concentration that their interactions with other clusters play an important role in the kinetics, then these particular clusters should be listed as separate components. In this way, our treatment becomes more generally applicable.

Since all of the basic ideas are contained in Reiss's publication, very little explanation of the physics is required here. The rate of nucleation, I^*, is determined by a pseudo-stationary state procedure which is reminiscent of the Eyring Theory of Absolute Rates. Or, better yet, it is reminiscent of Keck's Variational Theory of Reaction Rates.[8] Here the critical embryo (indicated by a subscript "c") corresponds to the "activated state;" the composition of an embryo (containing $n_1,\ldots,n_q$ molecules of components $1,\ldots,q$ respectively) corresponds to the interatomic separations; and $\Delta G(n_1,\ldots,n_q)$, the Gibbs free energy of formation of the embryo, corresponds to the potential energy surface.

Our objective is to provide a simple expression for the rate of nucleation. There are many ways in which our formalism could be improved at the expense of simplicity. It would be easy to: (1) use finite differences in place of derivatives; (2) determine the free energy in the critical nucleation region through the third order; and (3) correct the rate of nucleation for the curvature of the reaction path. However, it would be difficult to modify the formulation so as to take into account the nonequilibrium effects such as:[2-7] (1) time lag in the development of the critical nuclei; (2) the heating of the nuclei due to the exothermic energies of condensation and the cooling due to evaporation and heat transfers; (3) diffusion of molecules on the surface of nuclei to get into more favorable configurations; and oscillations of the nuclei. In spite of its crudeness, this type of classical nucleation kinetics agrees remarkably well with experimental results. This agreement is due, of course, to the fact that the nucleation occurs so suddenly as a function of the saturation that a factor as large as 100 or 1000 in the rate of nucleation is hardly noticeable.

I. THERMODYNAMICS CONSIDERATIONS

For an embryo of arbitrary size and composition, the free energy of formation is

$$\Delta G(n_1,\ldots,n_q) = G(n_1,\ldots,n_q) - \sum_j n_j\mu_{j0}(n_1,\ldots,n_q) \qquad (1)$$

where the $\mu_{j0}(n_1,\ldots,n_q)$ is the chemical potential per molecule of the j-th component in the mother phase outside of the embryo calculated at the ambient pressure and temperature, P_0 and T_0, assuming that this mother phase had the same composition as the embryo. The free energy of the embryo, $G(n_1,\ldots,n_q)$, can be determined á priori by combining quantum mechanical, statistical mechanical, and Monte Carlo techniques; or, the free energy can be approximated in terms of the properties of the bulk material.[9-11] The simplest approximation is the one which is usually used in the classical theory of nucleation,[1]

$$G(n_1,\ldots,n_q) = \gamma S_n + \sum_j n_j \mu_{jn}(n_1,\ldots,n_q) \tag{2}$$

Here $\mu_{jn}(n_1,\ldots,n_q)$ is the chemical potential per molecule of the j-th component of the bulk material having the same phase and composition as the embryo, and having the same pressure as the inside of the embryo; γ is the surface tension corresponding to a plane boundary which has, on one side the bulk material having the same phase and composition as the nucleus--on the other side is material having the same phase and composition as the system before nucleation; and finally, S_n is the surface area of the embryo which can be approximated by[1]

$$S_n = (4\pi)^{1/3} \left[3 \sum_j n_j \bar{v}_{jn}(n_1,\ldots,n_q)\right]^{2/3} \tag{3}$$

where $\bar{v}_{jn}(n_1,\ldots,n_q)$ is the partial molal volume per molecule of the bulk material having the same phase and composition as the embryo.

We assume that initially there are N_j $(j = 1,\ldots,q)$ single molecules per unit volume in the mother phase. During the nucleation period, but after the initial transients have disappeared, a pseudo-stationary concentration $N(n_1,\ldots,n_q)$ of embryos is maintained by the chemical kinetics. Furthermore, we assume that the nucleation period is sufficiently short that the concentration of single molecules is not appreciably depleted. Following Reiss's thermodynamical arguments, the concentration of embryos in thermodynamical equilibrium with these single molecules is[1]

$$N_e(n_1,\ldots,n_q) \;=\; \Big(\sum_j N_j\Big)\,\exp[-(kT)^{-1}\Delta G(n_1,\ldots,n_q)] \qquad (4)$$

Instead of expressing the composition of an embryo in terms of its components $(n_1,\ldots,n_q)$, we can express it in terms of a new set of components $(y_1,\ldots,y_q)$ where y_j corresponds to a "rotation" of the n_j-coordinate axes. Thus,

$$n_j \;=\; \sum_{i=1}^{q} U_{ji}y_i \quad \text{or} \quad y_i \;=\; \sum_{j=1}^{q} U_{ji}n_j \qquad (5)$$

Here $\underset{\approx}{U}$ is a unitary matrix which varies slowly with the total number of molecules in the embryo, $n = \sum_{j=1}^{q} n_j$. In keeping with the reaction kinetics analogy, we define y_1 to correspond to the distance along the "reaction path". The coordinates $y_2,\ldots,y_q$ then correspond to the internal (vibrational and rotational) modes orthogonal to the reaction path. Thus, y_1 might be defined as a locus of points for which the value of ΔG, corresponding to the composition $(y_1,0,\ldots,0)$, is a minimum when compared to ΔG for a nucleus having the same number of molecules but a slightly different composition. It is this definition of y_1 which makes $\underset{\approx}{U}$ vary slowly with y_1.

However, the principal concern of the theory of nucleation is the embryos whose composition is close to that of the critical embryo. The critical embryo can be defined as the composition corresponding to a saddle-point on the free energy surface. If there is no saddle-point, special techniques are required (analogous to the treatment of three-body atomic recombination reactions) which are beyond the scope of our present paper.

Since the critical embryo (designated by a subscript "c") is a saddle-point, all of the first derivatives of ΔG vanish,

$$\left(\frac{\partial \Delta G}{\partial y_j}\right)_c = 0 \quad \text{or} \quad \left(\frac{\partial \Delta G}{\partial n_j}\right)_c = 0 \,, \quad j = 1,\ldots,q \tag{6}$$

Furthermore, we can define $\underset{\approx}{U}$ at the saddle-point so that

$$\left(\frac{\partial^2 \Delta G}{\partial y_i \partial y_j}\right)_c = Q_i \delta_{ij} \,, \quad i \text{ and } j = 1,\ldots,q \tag{7}$$

where Q_1 is negative and all of the $Q_2,\ldots,Q_q$ are positive. Thus, the unitary matrix satisfies the conditions

$$0 = \sum_{u,v} U_{ui}U_{vj}\left(\frac{\partial^2\Delta G}{\partial n_u \partial n_v}\right)_c = \left(\frac{\partial^2\Delta G}{\partial y_i \partial y_j}\right)_c , \quad i \neq j \tag{8}$$

Of course, $\underset{\sim}{U}$ satisfies the unitary conditions

$$\sum_j U_{ij}U_{jv} = \delta_{iv} = \sum_j U_{ji}U_{jv} \tag{9}$$

Thus, $U^{-1}_{ji} = U_{ij}$. The specification of the $\underset{\sim}{U}$ is then completed by requiring that of the q constants

$$Q_i = \sum_{j,v} U_{ji}U_{vi}\left(\frac{\partial^2\Delta G}{\partial n_j \partial n_v}\right)_c , \tag{10}$$

the Q_1 is the negative one. Any residual indeterminancy in the $\underset{\sim}{U}$ is inconsequential for our purposes.

Thus in the vicinity of the critical embryo,

$$\Delta G = \Delta G_c + \tfrac{1}{2}Q_1(y_1 - y_{1c})^2 + \tfrac{1}{2}\sum_{i=2}^{q} Q_i y_i^2 + \ldots \tag{11}$$

Substituting Eq. (11) into Eq. (4), the equilibrium population of the embryo in the critical region is

$$N_e = N_{ec} \exp[-(2kT)^{-1} \{Q_1(y_1 - y_{1c})^2 + \sum_{i=2}^{q} Q_i y_i^2 + \ldots\}] \quad (12)$$

where the equilibrium concentration of critical nuclei is

$$N_{ec} = (\sum_j N_j) \exp[-\Delta G_c/kT] \quad (13)$$

II. PSEUDO-STATIONARY TREATMENT OF THE KINETICS

We assume that each of the embryos $A(n_1,\ldots,n_j,\ldots,n_q)$ of species $(n_1,\ldots,n_j,\ldots,n_q)$ can react with single molecules A_j of species j to form nuclei of species $(n_1,\ldots,n_j+1,\ldots,n_q)$,

$$A(n_1,\ldots,n_j,\ldots,n_q) + A_j \underset{k_j'(n_1,\ldots,n_q)}{\overset{k_j(n_1,\ldots,n_q)}{\rightleftharpoons}} A(n_1,\ldots,n_j+1,\ldots,n_q) \quad (14)$$

The reaction rates k_j can be expressed in the form

$$N_j k_j(n_1,\ldots,n_q) = \alpha_j \beta_j S_n(n_1,\ldots,n_q) \quad (15)$$

where S_n is the surface area of the nucleus, α_j is the probability that a molecule of j hitting the surface will stick, and β_j is the rate at which a molecule of j hits a unit surface area of the nucleus. For example, if the mother phase is considered to be a perfect gas,

$$\beta_j = p_j(2\pi m_j kT)^{-1/2}$$

where p_j is the partial pressure of j in the mother phase and m_j is the mass of a molecule of j. Frequently, α_j is taken to be unity.

The net rate of increase of species $(n_1,\ldots,n_j+1,\ldots,n_q)$ by means of the reaction given by Eq. (14) is

$$\begin{aligned} I_j(n_1,\ldots,n_q) &= k_j(n_1,\ldots,n_q)N_jN(n_1,\ldots,n_j,\ldots,n_q) \\ &\quad - k_j'(n_1,\ldots,n_q)N(n_1,\ldots,n_j+1,\ldots,n_q) \end{aligned} \tag{16}$$

But since

$$\begin{aligned} &k_j'(n_1,\ldots,n_q)N_e(n_1,\ldots,n_j+1,\ldots,n_q) = \\ &\qquad k_j(n_1,\ldots,n_q)N_jN_e(n_1,\ldots,n_j,\ldots,n_q) , \end{aligned}$$

if we define the ratios

$$f(n_1,\ldots,n_q) = N(n_1,\ldots,n_q)/N_e(n_1,\ldots,n_q) , \tag{17}$$

then Eq. (16) becomes

$$I_j(n_1,\ldots,n_q) = k_j(n_1,\ldots,n_q)N_jN_e(n_1,\ldots,n_j,\ldots,n_q) \times [f(n_1,\ldots,n_j,\ldots,n_q) - f(n_1,\ldots,n_j+1,\ldots,n_q)] \tag{18}$$

We can interpret I_j as the flux in the direction of increasing j of embryo having a fixed composition in all of the components except j. Thus, the net rate of increase of embryos of species $(n_1,\ldots,n_q)$ by means of <u>all</u> reactions with single molecules is

$$\frac{\partial N(n_1,\ldots,n_q)}{\partial t} = \sum_{j=1}^{q} [I_j(n_1,\ldots,n_j-1,\ldots,n_q) - I_j(n_1,\ldots,n_j,\ldots,n_q)] \tag{19}$$

For large nuclei, the finite differences in Eqs. (18) and (19) can be approximated by derivatives so that

$$I_j = -k_jN_jN_e(\partial f/\partial n_j) \tag{20}$$

and

$$\partial N/\partial t = -\sum_{j=1}^{q} (\partial I_j/\partial n_j) \tag{21}$$

If now we change the variables from the n_j to the y_i, then Eq. (21) becomes

$$\partial N/\partial t \;=\; -\sum_{i=1}^{q}\sum_{j=1}^{q} U_{ij}^{-1}(\partial I_j/\partial y_i) \;=\; \sum_{i=1}^{q}(\partial J_i/\partial y_i) \qquad (22)$$

where we have defined the functions J_i making use of Eqs. (16) and (20) so that

$$J_i \;=\; \sum_{j=1}^{q} U_{ij}^{-1} I_j \;=\; S_n N_e \sum_{u=1}^{q} B_{iu}(\partial f/\partial y_u) \;, \quad i = 1,\ldots,q \qquad (23)$$

in which we have defined

$$B_{iu} \;=\; \sum_{j=1}^{q} U_{ij}^{-1}\, \alpha_j \beta_j U_{ju} \qquad (24)$$

The J_i can be interpreted as the flux in the direction of increasing y_i of embryo with fixed composition in all of the y's except y_i .

This is the point where we make two key assumptions:

(1) During the nucleation period, the concentration of each species of embryo remains in a pseudo-stationary state so that $\partial N/\partial t = 0$ and Eq. (22) becomes

$$\sum_{i=1}^{q}(\partial J_i/\partial y_i) \;=\; 0 \qquad (25)$$

This ignores the initial induction period for the building up of the concentration and is a poor approximation when the nuclei are formed by very rapid chilling such as sometimes occurs when gases are expanded by flow through a nozzle.

(2) Since y_1 corresponds to the reaction path, the only nonvanishing component of the flux is in the y_1 direction. Thus,

$$J_2 = 0 \;, \quad J_3 = 0 \;, \quad \ldots \;, \quad J_q = 0 \tag{26}$$

Eq. (23) with $i = 2,\ldots,q$ forms a set of $(q-1)$ linear equations for the $(q-1)$ unknown variables $\partial f/\partial y_2,\ldots,\partial f/\partial y_q$,

$$-B_{i1}(\partial f/\partial y_1) = B_{i2}(\partial f/\partial y_2) + \ldots + B_{iq}(\partial f/\partial y_q) \;, \quad i = 2,\ldots,q \tag{27}$$

which has as its solution

$$\partial f/\partial y_u = \frac{(-1)^{u+1}}{D_2}(\partial f/\partial y_1) \begin{vmatrix} B_{21} & B_{22} & \cdots & B_{2,u-1} & B_{2,u+1} & \cdots & B_{2q} \\ \vdots & \vdots & & \vdots & \vdots & & \vdots \\ B_{q1} & B_{q2} & \cdots & B_{q,u-1} & B_{q,u+1} & \cdots & B_{qq} \end{vmatrix} \tag{28}$$

where D_2 is the determinant

$$D_2 = \begin{vmatrix} B_{22} & \cdots & B_{2q} \\ \vdots & & \vdots \\ B_{q2} & \cdots & B_{qq} \end{vmatrix} \tag{29}$$

Substituting Eq. (28) into Eq. (23) with $i = 1$, we obtain

$$J_1 = S_n N_e (D_1/D_2)(\partial f/\partial y_1) \qquad (30)$$

where D_1 is the determinant

$$D_1 = \begin{vmatrix} B_{11} & \cdots & B_{1q} \\ \vdots & & \vdots \\ B_{q1} & \cdots & B_{qq} \end{vmatrix} \qquad (31)$$

Eq. (30) can then be integrated along the reaction path y_1 to give

$$f = f_1 - \int_1^{y_1} \frac{D_2 J_1}{D_1 N_e} dy_1 \qquad (32)$$

Here f, J, and N_e correspond to the composition $y_1,\ldots,y_q$ and f_1 corresponds to the composition $y_1 = 1$ with the values of $y_2,\ldots,y_q$ the same as for the f, J, and N_e.

In order to proceed with the analysis, it is necessary to make three additional assumptions:

(1) For very small embryos corresponding to $y_1 = 1$, the concentrations of the embryos are very nearly in equilibrium with the concentrations of the single molecules. Thus, to a good approximation $f_1 = 1$.

(2) For very large embryo corresponding to $y_1 >> y_{1c}$ the concentration of embryo is negligible so that $f = N/N_e = 0$. This is reasonable.

(3) Since N_e becomes very small and varies very rapidly in the neighborhood of the critical point, most of the contribution to the integral in Eq. (32) comes from this region. Furthermore, the slowly varying functions D_2, D_1, and J_1 may be assigned their values corresponding to $y_1 = y_{1c}$ and taken outside of the integral sign. Actually, this is not a good assumption since the free energy surface in the vicinity of the saddle-point is usually slowly (instead of rapidly) varying, but fortunately this assumption does not make any large error in the predicted rate of nucleation.

With these assumptions and the use of Eq. (12), Eq. (32) becomes

$$\begin{aligned} 1/J_1 \;=\; & D_2[D_1 S_n N_{ec}]^{-1} \exp[(2kT)^{-1} \sum_{i=2}^{q} Q_i y_i^2] \\ & \times \int_1^{y_1 >> y_{1c}} \exp[(2kT)^{-1} Q_1 (y_1 - y_{1c})^2] dy_1 \end{aligned} \qquad (33)$$

The rate of nucleation is then given by

$$J^* = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} J_1 \, dy_2 \ldots dy_q \qquad (34)$$

Here the range of $-\infty$ to ∞ is suppose to imply the full range of the coordinates $y_2, \ldots, y_q$ holding $y_1 = y_{1c}$. If we now add the further assumption that S_nD_1/D_2 varies slowly as compared to the $\exp[-(2kT)^{-1} Q_i]$, then the factor S_nD_1/D_2 can be brought outside the integrations. Furthermore, since $(2kT)^{-1} Q_1$ is suppose to be negative and large in magnitude, to a good approximation

$$\int_{1}^{y_1 >> y_{1c}} \exp[(2kT)^{-1} Q_1(y_1 - y_{1c})^2]dy_1 = [-2\pi kT/Q_1]^{1/2} \qquad (35)$$

and

$$\int_{-\infty}^{\infty} \exp[-(2kT)^{-1} Q_i y_i^2]dy_i = [2\pi kT/Q_i]^{1/2} \qquad (36)$$

Thus, the rate of nucleation is

$$J^* = (2\pi kT)^{(q-2)/2} [N_e S_n D_1/D_2]_c [-Q_1]^{1/2} [Q_2,\ldots,Q_q]^{-1/2} \qquad (37)$$

Example: Two Components, $q = 2$.

Our present treatment agrees with the two-component nucleation formulation of Reiss[1] (and Mirabel and Katz's application of Reiss's method to sulphuric acid or nitric acid nucleation[12]). For the two-component nucleation, U is the two-dimensional rotation matrix with

$$U_{11} = \cos\phi = U_{22} \quad \text{and} \quad U_{21} = \sin\phi = -U_{12} \qquad (38)$$

Eq. (8) then becomes

$$\tan(2\phi) = 2\left(\frac{\partial^2 \Delta G}{\partial n_1 \partial n_2}\right)_c \Big/ \left[\left(\frac{\partial^2 \Delta G}{\partial n_1{}^2}\right)_c - \left(\frac{\partial^2 \Delta G}{\partial n_2{}^2}\right)_c\right] \tag{39}$$

in agreement with Eq. (8c) of Ref. (5). Also, from Eq. (10),

$$Q_1 = \left(\frac{\partial^2 \Delta G}{\partial n_1{}^2}\right)_c \cos^2\phi + 2\left(\frac{\partial^2 \Delta G}{\partial n_1 \partial n_2}\right)_c \sin\phi \cos\phi + \left(\frac{\partial^2 \Delta G}{\partial n_2{}^2}\right)_c \sin^2\phi \tag{40}$$

$$Q_2 = \left(\frac{\partial^2 \Delta G}{\partial n_1{}^2}\right)_c \sin^2\phi - 2\left(\frac{\partial^2 \Delta G}{\partial n_1 \partial n_2}\right)_c \sin\phi \cos\phi + \left(\frac{\partial^2 \Delta G}{\partial n_2{}^2}\right)_c \cos^2\phi \tag{41}$$

There are two solutions for ϕ which satisfy Eq. (39). We choose the root such that Q_1 is negative and Q_2 is positive. Then Eqs. (40) and (41) are in agreement with Eqs. (8a) and (8b) of Ref. 12 where $P = Q_1$ and $Q = Q_2$.

Now, using Eqs. (24) and (38), it follows that

$$\begin{aligned} B_{11} &= \alpha_1\beta_1 \cos^2\phi + \alpha_2\beta_2 \sin^2\phi , \\ B_{22} &= \alpha_1\beta_1 \sin^2\phi + \alpha_2\beta_2 \cos^2\phi = D_2 \\ B_{12} &= [-\alpha_1\beta_1 + \alpha_2\beta_2]\sin\phi \cos\phi = B_{21} \end{aligned} \tag{42}$$

And so

$$D_1 = \alpha_1\beta_1\alpha_2\beta_2 \tag{43}$$

Thus, the rate of nucleation as given by Eq. (37) is

$$J^* = (N_1 + N_2)\left[\frac{\alpha_1\beta_1\alpha_2\beta_2 S_n \exp[-\Delta G/kT]}{\alpha_1\beta_1 \sin^2\phi + \alpha_2\beta_2 \cos^2\phi}\right]_c \left(-\frac{Q_1}{Q_2}\right)^{1/2} \tag{44}$$

Here Eq. (44) agrees with the corresponding Eq. (87) of Ref. 1 and Eq. (6) of Ref. 12.

ACKNOWLEDGEMENTS

The author wishes to thank Howard Reiss and Joseph L. Katz for many helpful discussions.

REFERENCES

[*] The author would like to acknowledge research support from NASA Grant NGL 50-002-001 to the University of Wisconsin-Madison Theoretical Chemistry Institute; ARPA Grant DA-ARO-D31-G179 to the Quantum Institute of the University of California, Santa Barbara; and the Department of Chemistry, University of California, Santa Barbara.

1. H. Reiss, J. Chem. Phys. 18, 840 (1950).
2. A. Kantrowitz, J. Chem. Phys. 19, 1097 (1951).
3. W. G. Courtney, J. Chem. Phys. 36, 2009 (1962).
4. R. P. Andres and M. Boudart, J. Chem. Phys. 42, 2057 (1965); see also, R. P. Andres, Nucleation edited by A. C. Zettlemoyer, (Dekker, New York, 1969), Chap. 2.
5. F. F. Abraham, J. Chem. Phys. 51, 1632 (1969); see also F. F. Abraham, Homogeneous Nucleation Theory (Academic Press, New York, 1974), Sec. 5.5.
6. H. L. Frisch and C. C. Carlier, J. Chem. Phys. 54, 4326 (1971).
7. E. E. Salpeter, J. Chem. Phys. 58, 4331 (1973).
8. J. C. Keck, Adv. Chem. Phys. 13, 85 (John Wiley, New York, 1967); J. Chem. Phys. 32, 1035 (1960) and 29, 410 (1958). See also, E. P. Wigner, J. Chem. Phys. 5, 720 (1937).
9. J. Frenkel, J. Phys. 1, 315 (1939) and J. Chem. Phys. 7, 200 (1939); W. Band, J. Chem. Phys. 7, 324, 927 (1939); and A. Bijl, Ph.D. Dissertation, University of Leiden (1938).

10. F. P. Buff, J. Chem. Phys. 19, 1591 (1951). See also, M. Blander, D. Hegenstenberg, and J. L. Katz, J. Phys. Chem. 75, 3613 (1971).

11. F. F. Abraham, Homogeneous Nucleation Theory (Academic Press, New York, 1974), Chap. 4.

12. P. Mirabel and J. L. Katz, J. Chem. Phys. 60, 1138 (1974). Note that these authors point out a small error in G. J. Doyle, J. Chem. Phys. 35, 795 (1961).