Among the students who have participated in this program are: Billy M. Tolar, presently teaching PSSC physics at Thomas Jefferson High School in Port Arthur, Texas; Maurice L. Blackmon, NSF Fellow at MIT; Jon Holder, graduate assistant at University of Illinois; and J. Larry Verble, graduate assistant at the University of Iowa.

Homogeneous Nucleation of Vapor Condensation. II. Kinetic Aspects*

JAMES E. McDONALD
Institute of Atmospheric Physics, The University of Arizona, Tucson, Arizona

(Received 14 February 1962)

In the absence of foreign nucleants, phase transition from vapor to liquid is blocked by a free-energy barrier implicit in the appearance of new surface when embryos of the new phase start to form. Drawing upon thermodynamic relationships discussed in Part I, Part II here summarizes the kinetics of the homogeneous nucleation process for the case of the vapor-to-liquid phase transition. Emphasis is placed upon physical interpretation of the mathematical model used to obtain a nucleation rate equation for the unbalanced steady-state case.

I. INTRODUCTION

WHEN vapor is cooled to its nominal saturation point or when a liquid is cooled to its nominal solidification point, the answer to the question of whether phase transition will or will not immediately occur is dependent upon whether or not nucleation of the new phase can take place. In the absence of all foreign surfaces or particles (heterogeneous nucleants) phase transition does not occur until some finite degree of supersaturation or supercooling has developed.

The thermodynamic aspects of the latter mode of *homogeneous nucleation* were examined in Part I of this discussion, using vapor condensation as the example.[1] It was pointed out there that as soon as an embryonic liquid droplet of radius r and density ρ appeared in initially supersaturated vapor at pressure p and temperature T, the free-energy of the system is elevated by amount

$$\Delta F = 4\pi r^2\sigma - (4/3)\pi r^3 \rho RT \ln S, \qquad (1)$$

where σ is the specific surface-free-energy (identical with the surface tension in the case of liquids), R is the gas constant per gram of vapor, and S is the supersaturation ratio equal to p/p' if p' is the saturation vapor pressure at temperature T. (Certain limitations were noted in Part I concerning use of bulk values of σ for very tiny aggregates of molecules and these restrictions should be kept in mind in the following.)

We saw, furthermore, that for $S>1$, ΔF passes through a maximum

$$\Delta F^* = 16\pi\sigma^3/3(\rho RT \ln S)^2 \qquad (2)$$

at some embryo radius, defined to be the *critical radius* r^*, satisfying the Kelvin equation

$$r^* = 2\sigma/\rho RT \ln S. \qquad (3)$$

Those thermodynamic considerations posed this dilemma: Although supersaturated vapor is in a metastable state because its specific-free-energy exceeds by the finite amount $RT(\ln S)$ that of liquid at the same temperature, it cannot jump to the preferred lower free-energy state because that jump can only proceed via formation of tiny drops, beginning with clusters of two, three, four molecules etc.; and growth of such embryos of the new phase carries the system up to states where the total free-energy of the system has, according to (2), *risen* more by creation of new surface-free-energy of the embryonic drops than it has *fallen* by virtue of the bulk-free-energy change accompanying the phase transition that produced those drops. That is, phase transition is always, in the homogeneous case, blocked by an activation energy barrier (which unlike the potential barriers of nuclear physics will not permit tunneling at any significant rate, this being a classical process).

---

* Supported in part by the Office of Naval Research.

[1] J. E. McDonald, Am. J. Phys. **30**, 870 (1962).

Inspection of (2) and (3) suggested the only possible way out of this dilemma: If we can raise S high enough, we shall lower the height ΔF^* of the activation-free-energy barrier standing in the way of phase transition; or viewing it slightly differently, we thereby lower r^*, the critical embryo radius which must be exceeded in order that our system will *spontaneously* shift to the preferred state of lowest possible free-energy. A further clue to the way nature finally, at some high S, gets over the barrier was found in the important fact that in subsaturated vapors there actually exists, as a statistically steady population, a distribution of embryos satisfying a Boltzmann-type relation[2]

$$n_g = n_1 e^{-\Delta F_g/kT}, \tag{4}$$

in which n_g is the number of clusters of g molecules, and ΔF_g is obtained from (1) by a straightforward interchange of r and g as the size parameter. If fluctuation phenomena can, even at $S<1$, support such a population of molecular clusters, then when S rises *above* unity, we should surely expect a general increase in that population at all g, since raising S raises growth rates and also lowers ΔF_g for any given g. Hence, for some large S (theory and observation[3] both suggest values around 5 or 6 for this S) we can expect to reach a point where fluctuations can send some favored embryo or embryos over the top of the free-energy barrier whereupon the supercritical embryos can subsequently grow without limit until the vapor pressure is pulled from p down to p' and the system is thermodynamically stabilized.

In this second part of the discussion, we examine the *kinetics* of the growth and decay of embryos and describe a model that, although somewhat artificial, provides a working model of homogeneous vapor nucleation and makes possible at least rough estimates of the degree to which S must be raised to initiate phase transition. This summary draws upon ideas and methods of analysis developed by Frenkel,[4] Zeldovitch,[4] and Farley,[5] but the interpretation includes a number of viewpoints that are the writer's.

II. RATES OF GROWTH AND DECAY OF EMBRYOS

A spherical embryo of arbitrary radius r is bombarded by vapor molecules at a rate $C=4\pi r^2 b$, where $b=n\bar{v}/4$ and n is the molecular density of the vapor, $\bar{v}$ the mean molecular speed. Of all those molecules hitting the embryo only some fraction q will stick, where q is the *condensation coefficient.* Using the expression for $\bar{v}$ given by kinetic theory, b may be put into such a form that we have condensation rate

$$C = 4\pi r^2 qp/(2\pi mkT)^{\frac{1}{2}}, \tag{5}$$

where m is the mass of one vapor molecule and p is the prevailing (supersaturated) vapor pressure. For the rate of escape E of molecules leaving the same embryo, we may write

$$E = C^*, \tag{6}$$

where C^* is the value given by (5) when we therein change p to that particular value for which the *given* embryo radius would represent the critical radius. The somewhat subtle basis for this assertion is that E has such a value that it would be just equilibrated by the condensation rate that would prevail *if* that same size of embryo were in metastable equilibrium with respect to vapor of that particular pressure which would satisfy (3) with r substituted for r^*. Briefly, (6) is based upon an equilibrium argument.

Combining (5) and (6) we find, after making suitable use of (3), that the ratio of escape to condensation for embryos of radius r satisfies the simple relation

$$E/C = S^{(r^*-r)/r}, \quad S>1 \tag{7}$$

which displays the important point that embryos of *subcritical* size fight an uphill battle because their evaporation rates exceed their growth rates. The latter is only a statement of *average* conditions, however, and occasional fluctuations in collision and escape rates permit a rare embryo to grow to surprising size, contributing momentarily to a mean distribution of the form of (4). A large value of S might seem from (7) alone to be unfavorable to growth, but this is

---

[2] J. Frenkel, *Kinetic Theory of Liquids* (Dover Publications, New York, 1955), p. 380.

[3] B. J. Mason, *The Physics of Clouds* (Oxford University Press, London, 1957), p. 13.

[4] See reference 2, pp. 368 ff.

[5] F. J. M. Farley, Proc. Roy. Soc. (London) **A212**, 530 (1952).

deceptive since S enters r^* in such a way that its effect in reducing r^* and ΔF^* more than compensates by lowering the distance to and height of the barrier; so as S rises the chance of a really favorable sequence of events sending some favored embryo over the top is enhanced. Note from (7) that, as we would expect from arguments given in Part I, the balance condition $E=C$ is satisfied when $r=r^*$, while for still greater r we have $C>E$, i.e., an embryo, having become *supercritical*, should keep right on growing until it has become a drop of molecularly huge dimensions. (This supercritical stage of embryo growth is very closely analogous to the synthesis of the heavy atoms beyond bismuth in a supernova, as recently elucidated by Fowler, Hoyle, and others.[6] In the presence of the high neutron-density characteristic of a supernova, neutrons are added faster than alpha-decay can reduce nuclear masses, with the result that rapid synthesis out to mass numbers near 260 ensues, limited finally by spontaneous fission. Supercritical embryos experience a similar excess of growth over decay, as in the case of the man who can't spend money as fast as he can make it.)

In the following sections we shall find it more convenient to identify embryo sizes through g rather than r since we shall be considering rates of addition and removal of individual molecules. Thus, by replacing r by g in (5) and (6) through the identity $(4/3)\pi r^3\rho = gm$ we may speak of the condensation rate C_g and evaporation rate E_g of a g-mer.

The writer has found that examination of computed magnitudes of C_g and E_g for specific cases proves rather illuminating. In Fig. 1 are plotted curves showing the variation of these two opposing rates for embryo sizes up to $g=200$ for water vapor at 0°C and for one particular supersaturation ratio, $S=4.0$. The condensation coefficient q has been taken as 1.0 for simplicity (The lowest existing estimates[7] of q for water vapor are of order 0.01, so the absolute values of all points might run as much as two orders of magnitude lower than plotted, but this need not concern us here.) With p and T fixed, C_g, on present assumptions, varies only as the embryo's surface area (i.e., as $g^{\frac{2}{3}}$), hence the curve for C_g rises monotonically as shown. The curve for E_g, however, is seen to pass through a minimum near $g=30$, a consequence of joint action of the geometric factor just considered for C_g and the opposing influence of the initially very rapid fall-off in intrinsic escape rate as we build up the embryo size from extremely small values. The sharp initial decrease in escape rate may be viewed molecularly as due to a rapid rise in net work of escape as we increase numbers of near neighbors, an effect that is initially very marked.

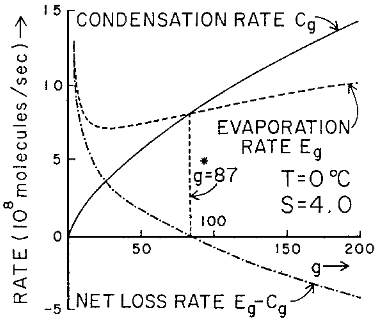

FIG. 1. Variation of condensation and evaporation rates with embryo size g. Case shown is for water vapor at 0°C, $S=4.0$.

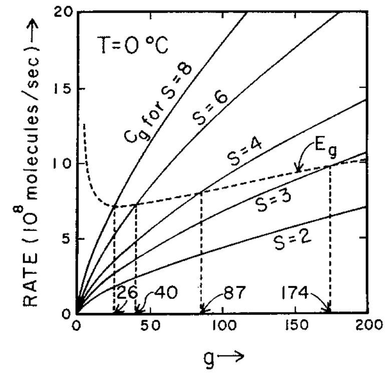

FIG. 2. Effect on g^* due to varying S at fixed T.

Also plotted in Fig. 1 is a curve for the net excess of evaporation over condensation. That curve displays the basically important point that this excess is large for small g, but finally vanishes at the cross-over point of the C_g and E_g curves, and goes negative beyond that point, which is the critical point, of course. For the case shown in Fig. 1, the net rate of loss vanishes at $g=87$ molecules, whence $g^*=87$ for this case.

If we hold T fixed, but vary S, the curve for

---

[6] W. A. Fowler, Sci. Monthly **84**, 84 (1957).

[7] T. Alty and C. A. Mackay, Proc. Roy. Soc. (London) **A149**, 104 (1935).

E_g remains unchanged since escape rates are controlled only by temperature and by embryo size. By plotting a set of C_g curves for $T=0°\mathrm{C}$ and for several values of S from 2 to 8, Fig. 2 was obtained. The cross-over points for each curve are the respective g^* values, when referred to the abscissa. Comparison with Table II of Part I will show agreement with the g^* values calculated there from explicitly thermodynamic considerations. In Fig. 2, the C_g curve for $S=2$ would not intersect the E_g curve until we moved out to $g=695$, an embryo of such enormous size, by present standards, that it could only occasionally form in a huge vapor volume (see Sec. V). From the ordinate scales of Fig. 1 and Fig. 2 note that embryo growth and decay is a very lively affair. The mean lifetime of a g-mer of some specified size near g^*, where the absolute value of the net loss rate is of order 10^8 sec^{-1}, is only about *0.01 microsecond.* Within that time, the g-mer will, on the average, have gained or lost a molecule, thereby moving out of its previous g-class. We turn, in the next section, to more general considerations of this chaotic exchange of molecules between the g-mer population and the reservoir of free molecules in the vapor phase.

III. UNBALANCED, NONSTEADY-STATE EMBRYO GROWTH

When a body of vapor has just been compressed isothermally to a supersaturated state, or, as in expansion cloud chambers, has just been expanded adiabatically to such a state, there will be a brief transient period in which the embryo population is being built up by collisional processes. Although it is not easy to analyze mathematically such a transient state, it helps in fixing ideas and in introducing needed concepts to formulate the equation governing such an *unbalanced, nonsteady-state case.*

Considering any g, embryos of that size can be *created* either by addition of a molecule to some $(g-1)$-mer or by evaporative loss of a molecule from some $(g+1)$-mer. Concurrently, g-mers can be *destroyed* either by growing into $(g+1)$-mers by addition of a molecule or by decaying into $(g-1)$-mers through loss of a molecule. Denoting by N_g the concentration of embryos of size g at any instant, and approximating a difference equation with a differential equation, we may write

$$\partial N_g/\partial t=(C_{g-1}N_{g-1}+E_{g+1}N_{g+1})-(C_gN_g+E_gN_g).$$

Defining I_g to be the following *net* rate,

$$I_g=C_gN_g-E_{g+1}N_{g+1} \tag{8}$$

we can write

$$\partial N_g/\partial t=I_{g-1}-I_g. \tag{9}$$

Equation (9) permits concise specification of the distinction between the general unbalanced nonsteady-state case just considered and two other cases which we wish to consider below in detail: The *steady-state* cases will be those in which N_g does not change with time because the I_g have one and the same value for all g. If, in particular that constant value of I_g is simply *zero*, then we have the *balanced* steady-state case of the next section. Somewhat more generally, I_g may exhibit some constant. *nonzero* value I for all g, in which case we have the *unbalanced* steady-state case which forms the basis of the model used below to approximate actual nucleation processes. Equation (9) is, of course, merely a continuity statement contingent upon conservation of molecules within the embryo chain; and we may speak of I_g as the "current" of embryos flowing across the link between $(g-1)$-mers and g-mers in our population.

Farley[5] treats the unbalanced nonsteady-state equation (9) under simplifying approximations and obtains as a crude estimate of the transient-time to build up the populations to 90% of the quasi-steady-state value a time of the order of tens of microseconds, i.e., brief enough compared to expansion times of cloud chambers that we may ignore the transient phase in such experimental situations. In shock condensation phenomena in supersonic wind tunnels, however, the entire expansion period may be only of the same order of magnitude as this transient period, so conventional nucleation theory is somewhat less confidently applied in the latter instances. Here our concern will be limited to instances of the former type where we shall be able to ignore the time required to build up the embryo population to very nearly its steady-state distribution so (9) will not directly enter our further discussions.

IV. BALANCED STEADY-STATE CASE

If, in (9), we specify that $I_g=0$ for all g, then the N_g are no longer variable with time since the "current" vanishes everywhere due to local balance at *each* link of the embryo chain. This is just the condition for thermodynamic equilibrium; so we may here identify N_g with the n_g of the Boltzmann-type distribution given by (4), with one proviso: For $S>1$, the case of interest to us, ΔF exhibits a maximum, whence, by (4), n_g exhibits a minimum at g^*, the critical embryo size measured in number of constituent molecules. The existence of the latter minimum is, *per se*, acceptable, but we are embarrassed to note that (4) then implies that n_g *rises* exponentially for $g>g^*$. To preserve a semblance of physical meaning we may introduce an artifice: We equip a nimble-footed Maxwell's demon with a perfectly reflecting surface and have him dart about reflecting back into embryos of some given size $g'>g^*$ each molecule that evaporates from a g'-mer. This task performed, our distribution simply cuts off at g', and the balanced steady state is maintained without the catastrophe of having an infinitely large system. The obligation of introducing the idea of a reflecting barrier terminating the embryo chain at g' removes direct physical meaning from our balanced steady state for $S>1$, of course, but its mathematical meaning is clear. This hypothetical population can be used to obtain further insight into the real problem of nucleation and will prove very useful in the mathematical analysis of our third case of the unbalanced steady-state embryo chain with I constant but nonzero.

TABLE I. Values of J_g for two supersaturation ratios S.

g	5	10	15	20	25	50	100
$S=1.0$	43	16	12	9.3	8.0	5.2	3.8
$S=4.0$	10	4.1	2.9	2.3	2.0	1.3	0.94

Since (7) implies that, so long as $g<g^*$, $E>C$, it is relevant to ask how our present n_g distribution can be maintained steady for small g in the face of this intrinsic excess of evaporation over condensation. From (8) placing $I_g=0$ and substituting, correspondingly, n_g for N_g, we have for *all* links in this steady-state embryo chain of zero current,

$$C_g n_g = E C_{g+1} n_{g+1}. \tag{10}$$

Defining the ratio of the populations of neighboring g states as

$$J_g = n_g / n_{g+1} \tag{11}$$

we find from (4), on introducing a constant A such that the surface-free-energy term in (4) satisfies the identity $4\pi r^2\sigma = Ag^{\frac{2}{3}}$, and on noting g and R are so defined that $(4/3)\pi r^3 RT = gkT$, where k is the Boltzmann constant,

$$\begin{aligned} J_g &= S^{-1}\exp[(A/kT)\{(g+1)^{\frac{2}{3}} - g^{\frac{2}{3}}\}] \\ &\approx S^{-1}\exp[2A/3kTg^{\frac{1}{3}}], \end{aligned} \tag{12}$$

wherein the last form, obtained from use of a truncated binomial expansion, holds quite accurately for g greater than about 10. Using (12), some representative values of J_g for two different supersaturation ratios have been computed and are summarized in Table I. Consider first the case of $S=1$, which represents a *physically realizable* balanced steady-state case, as noted earlier. We see that there are over 40 times as many 5-mers per unit volume as 6-mers, and about 16 times as many 10-mers as 11-mers, with J_g falling towards larger g. Here is the clue to the maintenance of a steady state in face of the condition $E/C>1$: There are so many more small embryos than large ones that the *over-all* rates of formation of $(g+1)$-mers from g-mers can just balance the inverse process despite the condition $E>C$. Indeed, this balance condition is implicit in (10). But (12) and Table I tell us rather more than (10) when we consider what happens as S rises above unity. At $S=4$, we find all J_g decreased by a factor of four compared with $S=1$, with the result that for some g slightly less than 100 (direct calculation gives 87) $J_g=1$, and remains less than one for all greater g. Since the condition $J_g=1$ is the balance condition characterizing a critical embryo, we conclude that raising S to 4 implies $g^*=87$, as is confirmed by Table II of Part I. From the simple way in which S enters (12) we see that we can deduce further (from the values of J_g for $S=1$ in Table I) that the critical embryo size for, say $S=3.8$ must be $g^*=100$, or for $S=8.0$ is $g^*=25$, etc.

V. UNBALANCED STEADY STATE

The balanced steady state just considered, although interesting and even illuminating, does not afford a realistic model of nucleation because a *nonzero* current I is an essential requirement in any model of real nucleation processes. Strictly speaking, real cases of nucleation are precisely describable only in terms of the unbalanced nonsteady-state model and its differential equation (9). However, as a compromise with the mathematical difficulties inherent in coping directly with (9), clever use can be made of the fact that the transient time or relaxation time, as derived from (9) under crude but not meaningless simplification, is short compared with the characteristic times of many condensation processes. The consequence of the latter fact is this: In actual nucleation problems we can, to tolerably good approximation, divide the nucleation process into two periods, the very short initial period (transient state lasting of the order of tens of *microseconds* on Farley's theoretical estimate) when the embryo population is steadying off up to moderately large g, and a longer period (which may still be short by everyday standards, lasting perhaps tens to hundreds of *milliseconds* in expansion cloud chambers, for example) in which we may meaningfully speak of a quasi-steady rate of production of supercritical embryos at scattered points throughout the bulk of the vapor. This second period must be regarded as terminating when the condensational growth of these supercritical embryos begins to sensibly deplete the system of its excess vapor; for once the vapor pressure so falls, or the temperature rises due to latent heat effects, S begins to fall rapidly and the conditions defining our problem are no longer constant. However, once this many embryos have been generated during the second period, the nucleation process, *per se*, is accomplished. We simply are not here interested, that is, in the third and final period of rapid growth that lowers p to p'. That period is an episode of interest in the theory of *diffusional growth*, but not in the theory of nucleation.

The above considerations led early developers of nucleation theory to the idea of approximating the second crucial period in terms of a model in which the concentration of embryos of each size g, now denoted by a new distribution-function symbol f_g to avoid confusion with either N_g or n_g, does not change with time (steady state), but in which a uniform *nonzero* current I "flows" through the embryo chain due to a statistical excess of condensational growth over evaporative decay of embryos at *each* link of the chain. This comprises the *unbalanced steady-state* case upon which admittedly rough but still very useful estimates of I are based in nucleation theory.

To repeat, for emphasis, condensational formation of $(g+1)$-mers from g-mers can exceed evaporative decay of the $(g+1)$-mers *in spite of* the fact that $C_g < E_{g+1}$ for $g < g^*$ and *because of* dominant effect of the inequality $f_{g-1} > f_g$. Hence, I can be *positive* for all g within our range of concern (see below) and is now regarded as *constant* for all g in that range, since our *steady-state* stipulation requires that the imbalance at any given link be just counteracted by the same imbalance at the two links on either side of it in order to leave the f_g invariant with respect to time. That is,

$$I = C_1 f_1 - E_2 f_2 = C_2 f_2 - E_3 f_3 = \cdots$$
$$\cdots = C_g f_g - E_{g+1} f_{g+1} = \cdots = \text{constant.} \quad (13)$$

We now limit the g range with which we shall be concerned by invoking a notion due, according to Dunning,[8] to Szilard: We imagine some means whereby every embryo that succeeds in growing to size G, where G is rather larger than g^* (perhaps about twice g^*), is deftly removed from the system, broken down into G constituent molecules, and the latter re-inserted into the system to work their way up the embryo chain once more. The Szilard artifice maintains the steady state with only a finite number of molecules in the system and provides one boundary condition on our unknown f_g distribution, namely,

$$f_G = 0. \quad (14)$$

As will be shown *a posteriori*, the value of I inferred from the model is surprisingly insensitive to changes in G, so our choice of G is not critical.

At the beginning of our embryo chain we are able to introduce another useful approximation to reality. We saw in our discussion of the

---

[8] W. J. Dunning in *Chemistry of the Solid State*, edited by W. E. Gardner (Butterworths Scientific Publications London, 1955), pp. 159–183.

balanced steady-state case, that for small g the n_g, though small compared with n, were still large absolute numbers when referred to volumes of laboratory size (order of cubic centimeters). Hence, to produce a current I, whose value is as small as that required in real nucleation processes, we find from comparison of (10) with (13) that for very small g the f_g need differ only inconsequentially from the n_g of the balanced steady-state distribution corresponding to the same S and T in order that the distribution curve be steepened just enough to support any reasonable value of I.[9] Briefly, because n_g and f_g are so large for very small g, the two sets of populations satisfy, to high degree of approximation, the relation

$$\operatorname*{limit}_{g\to 1}(f_g/n_g)=1, \qquad (15)$$

which will provide us with our second boundary condition on f_g below, (14) being the first.

The next step is a crucial one, for when one reviews the whole analysis, this next step is seen to unlock the door to the prediction of I. That the following step is so important makes it a source of some dismay to the present writer that he has never quite been able to see why anyone would ever have thought of it in the first place, and he is unaware of exactly when in the history of nucleation theory this crucial trick was first noted. The trick consists of forcing into the analysis, in a way that is much less obvious than was the case in writing (14), the characteristics of the n_g distribution. Perhaps (15) suggested it; perhaps sufficient manipulation of the running equality of (13) led someone to recognize the simplification to be gained. In any event, the trick consists in rewriting the general term of (13) as

$$\begin{aligned} I&=C_gn_g[f_g/n_g-(E_{g+1}/C_g)(f_{g+1}/n_g)] \\ &=C_gn_g[f_g/n_g-f_{g+1}/n_{g+1}], \end{aligned} \qquad (16)$$

where the second form of the right member follows from the first form on making use of the balance equation (10) for the n_g model.[10] From (16) we obtain the series of equations

$$\begin{aligned} I/C_1n_1&=f_1/n_1-f_2n_2 \\ I/C_2n_2&=f_2/n_2-f_3/n_3 \\ &\vdots \qquad\qquad \vdots \\ I/C_{G-2}n_{G-2}&=f_{G-2}/n_{G-2}-f_{G-1}/n_{G-1} \\ I/C_{G-1}n_{G-1}&=f_{G-1}/n_{G-1} \end{aligned}$$

where boundary condition (14) has been used in the final equation of this series. On summing the left and right members, respectively, and using boundary condition (15), we have

$$\sum_{g=1}^{G-1}(I/C_gn_g)=f_1/n_1\doteq 1. \qquad (17)$$

In (17) note carefully that I is constant, though still unknown, that the characteristics of the unknown f_g distribution function have entirely disappeared (!), and that (17) effectively specifies our unknown I in terms of a finite series of reciprocals of form $1/C_gn_g$. Since both C_g and n_g are known functions of g, the device employed in (16) plus the Szilard boundary conditions at G and the asymptotic equivalence of f_g and n_g for small g have led us to the happy end of approximating I solely in terms of known quantities.

There remains now the task of finding the value of the sum in (17). Using a digital computer, this would be relatively easy, and the writer has done just this for several sets of experimental data as a means of gaining further insight into certain mathematical properties of the nucleation model (see below). However, it proves possible, as many previous workers have noted, to obtain a fairly precise answer by approximating our finite-difference description with a differential equation and then to use three further mathematical dodges to achieve our goal.

To make this shift in our mode of description we return to (16) and write (as a good approximation for those larger g values which prove to

---

[9] Here it is quite important to keep in mind that nucleation is actually accomplished by values of I (units of $\text{cm}^{-3}\,\text{sec}^{-1}$) that are extremely small when compared with collision frequencies measured in the same units.

[10] Use of (10) here might easily be misconstrued to imply that we have now restricted our model in some sense. In fact, however, (10) is brought in solely as an auxiliary mathematical identity; the sole restriction of importance remains the (rather good) approximation that f_g approaches n_g in the limit of very small g.

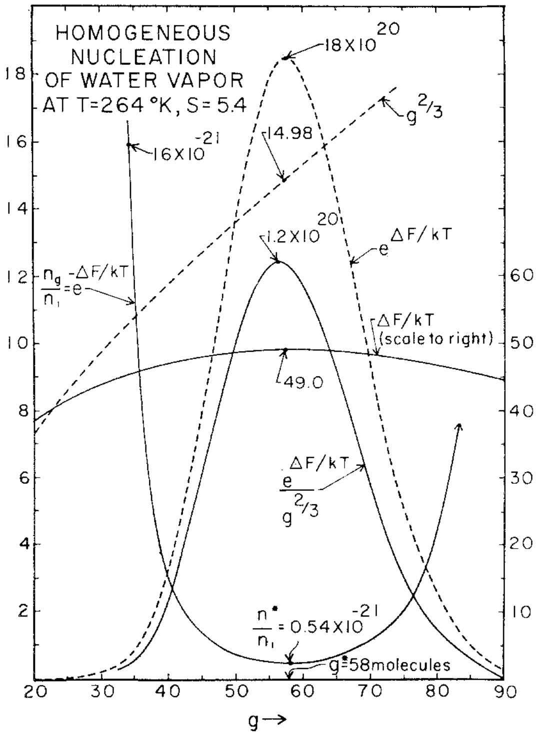

FIG. 3. Behavior of nucleation parameters in the critical region. Data refer to water vapor at 264°K, $S=5.4$, corresponding to experimental case studied by Barnard (see Mason[3]).

be of controlling importance),

$$I \doteq -C_g n_g \frac{d}{dg}(f_g/n_g),$$

a form that follows from the fact the smallest value of the denominator of the difference quotient corresponding to the derivative is here unity, the least amount by which g can be varied. Hence,

$$d(f_g/n_g) = -(I/C_g n_g)dg$$

which, on integrating from $g=1$ to $g=G$ yields, on introducing (14) and (15) as boundary conditions,

$$I = \left[\int_1^G dg/C_g n_g\right]^{-1}. \qquad (18)$$

(The writer would call the reader's attention to the interesting point that our problem of evaluating I is here exactly analogous to that of finding an unknown *steady-state heat-flux* through a slab for which the temperatures of both faces of the slab are constant and known. That is, we have here a two-point boundary-value problem with unknown flux.)

The integral in (18) is not expressible in terms of elementary functions, but use of three further approximations puts it into soluble form. The validity of the approximations can be better appreciated by studying Fig. 3, which represents plots of data pertaining to a particular expansion-chamber experiment due to Barnard and summarized by Mason.[11] These data were computed by the writer using an IBM 650 computer, as part of a finite-difference solution (*exact* solution!) of (17). If we replace r by g in (5) we see that C_g varies as $g^{\frac{2}{3}}$, which makes it a rather slowly varying function, as is clearly shown in Fig. 3. On the other hand, by (4), $(n_g)^{-1} = n_1^{-1} \times \exp(\Delta F/kt)$ is everywhere very small except in the neighborhood of g^*, where it passes through a sharp maximum, as depicted in Fig. 3. Thus, little error will be made by taking C_g outside the integral in (18) as a constant and evaluating it at g^*, a type of approximation found useful in more than a few problems of mathematical physics. This first of our three present approximations we then follow by expanding the exponential portion of $(n_g)^{-1}$ in a Taylor series about g^* where it passes through its maximum in a roughly symmetric manner (Fig. 3), i.e.,

$$\Delta F_g = \Delta F^* + \left[\frac{\partial(\Delta F)}{\partial g}\right]_{g^*}(g-g^*)$$
$$+\frac{1}{2}\left[\frac{\partial\ (\Delta F)}{\partial g^2}\right]_{g^*}(g-g^*)^2+\cdots. \qquad (19)$$

The coefficient of the second term of the Taylor series is zero since g^* is, by definition, that g for which $\partial(\Delta F)/\partial g$ vanishes (see Part I, and Fig. 3). On rewriting (1) with g replacing r as our variable, we find that the bracketed coefficient in the last term of our truncated Taylor series, the negative of which we will call Q is given by evaluation of the second derivative at g^* as

$$Q \equiv -\left[\frac{\partial^2(\Delta F)}{\partial g^2}\right]_{g^*} = (2/9)Ag^{*-4/3}, \qquad (20)$$

where A is as defined for Eq. (12).

With these approximations (18) becomes, on

---

[11] See reference 3, p. 17.

changing to a new variable of integration $x \equiv g - g^*$,

$$I^{-1} = \frac{e^{\Delta F^*/kT}}{C_{g^*}n_1} \int_{-(g^*-1)}^{G-g^*} e^{-Qx^2/2kT}dx. \qquad (21)$$

Inspection of Fig. 3 shows that there will be little change produced in the value of the integral in (21) if, as our third dodge, we now shift the lower limit of integration to $-\infty$ and the upper limit to $+\infty$, so long as g^* amounts to several tens of molecules and so long as G is greater than about twice g^*. With that change of limits (which is intended to convey no physical meaning at all, of course—it merely puts our integral into soluble form at the price of almost negligible numerical error), (21)becomes a known integral and writing n^* for $n_1 e^{-\Delta F^*/kT}$, we have

$$I = C_{g^*}n^*/(2\pi kT/Q)^{\frac{1}{2}}. \qquad (22)$$

Finally, using (5), (20) and the kinetic theory relation[12] $p = nkT$, (22) can be written in such alternative forms as

$$I = (n^2/\rho)(2\sigma m/\pi)^{\frac{1}{2}} e^{-\Delta F^*/kT} = (p/\rho kT)(2\sigma m/\pi)^{\frac{1}{2}} n^*. \qquad (23)$$

Appearance of n^2 as a factor in the equation for I displays the effectively second-order nature of the kinetics of nucleation, analogous to the n^2-dependence met in many coagulation, recombination, and chemical processes as well as in nucleosynthesis in stars. As we raise S, this factor rises as S^2, which helps to raise I. But that effect, so readily interpretable in straightforward kinetic terms, is relatively unimportant compared with the overwhelming effect of raising the value of the exponential factor in (23) as S rises. The latter effect, as has been stressed repeatedly above, dominates the kinetics as well as thermodynamics of nucleation by so lowering ΔF^* and reducing g^* that the system finally has an appreciable probability of overtopping the activation energy barrier and generating supercritical embryos at some detectable rate I.

Presence of n^* in the second expression for I in (23) must *not* be construed as meaning that our theoretical model is really based upon the n_g distribution with its implausible minimum at g^*. Despite the important *mathematical* consequences of introducing the n_g distribution function into (16), which succeeded, by the stage of analysis represented by Eq. (18), in completely hiding the f_g distribution from sight, our model and hence (23) *is* based upon the f_g distribution. In Fig. 3 the n_g distribution is plotted in the form of the n_g/n_1 ratio. A similar curve for the f_g distribution would lie everywhere *below* that plotted curve, and would cut the g axis at some $g = G$ off the right edge of the figure. It aids in getting a vivid picture of the rarity of formation of g-mers as large as g^* to realize that if we were to try to continue the plot of n_g/n_1 upward beyond the top of Fig. 3 until the curve approached $n_g/n_1 \doteq 1$ at $g = 1$, we would need a sheet of paper extending about 1000 light years above the top of Fig. 3, assuming it to be plotted on the same scale!

From the writer's digital-computer determinations of I, he found that the three approximations employed in evaluating the integral in (18) introduce an error of only about 1% compared with the "exact" value when G was taken as 200 for the case illustrated in Fig. 3. If, to give the model a slightly greater degree of reality, we shifted G from 200 down to say $g^* + 1 = 59$ molecules, the computer results revealed that the estimate of I would increase by a mere factor of 1.6, an utterly inconsequential variation of I in view of the fact that I changes by many orders of magnitudes as we make rather small variations in S itself. Indeed, the exercise of examining that point with the aid of the computer data called attention to the fact that one could have sensed directly from the geometric meaning of the modified integral of (21) that shifting G from infinity down to g^* would yield a reduction of I by a factor of 2.0 under the approximations leading to (21). The difference between the "exact" reduction factor of 1.6 and the theoretical estimate of 2.0 stems from the slope of the $g^{\frac{2}{3}}$ curve of Fig. 3. Because of that slope, rather more than half of the "exact" I-integral (I-sum to be precise) lies on the low side of g^*, so reducing G from infinity to g^* does not produce quite as much as a doubling of I.

That I *rises* as G is lowered is best understood

---

[12] Since $n_1 \gg n_2$, etc., we have, to very high degree of accuracy the relation $p = nkT$, with n taken as total number of molecules per unit volume, the union of a tiny fraction of those n into the several classes of g-mers scarcely influencing the pressure of the vapor.

TABLE II. Values of I and n^* for various S.

S	2	3	4	5	6	7	8
$I(\mathrm{cm}^{-3}\,\mathrm{sec}^{-1})$	4×10^{-82}	2×10^{-17}	5	2×10^{7}	3×10^{11}	1×10^{13}	4×10^{15}
$n^*(\mathrm{cm}^{-3})$	3×10^{-87}	1×10^{-24}	2×10^{-8}	0.6	8×10^{3}	3×10^{5}	8×10^{7}

by analogy with the two-point heat-conduction problem: For fixed boundary conditions, reducing the thickness of the slab raises the steady-state heat flux; and similarly for I here. That we get no more than a doubling of I for such large G changes serves to increase one's confidence in the physical meaning of the model employed. If we found the theoretical estimates of I to be strongly sensitive to where we picked that $g=G$ for which f_g was assumed to vanish we would be much more dubious of the usability of our results.

To display the marked variations of I that attend S variations within the experimental range encountered in cloud chamber expansions and in many other condensation phenomena, the values of Table II were computed for water vapor at 0°C, using (23). Also shown for reference are values of n^* from (2) and (4). Because of considerations of sensitive times of cloud chambers or transit times through condensation shocks, it becomes slightly more meaningful to deal with the reciprocal of I, which constitutes an "average time between nucleation events in unit volume." Using values from Table II, one finds that at $S=2$ (200% relative humidity, in meteorological phraseology) one would have to wait 10^{83} sec for a single supercritical embryo to form in one cubic centimeter of water vapor at 0°C. This is at least 10^{60} times the total age of the earth, which is a way of saying that homogeneous nucleation is essentially impossible at such "low" degrees of supersaturation. For $S=3$ the waiting time is still a discouraging 2×10^{11} years. If we try to trade volume for time, we find that a sphere of vapor at $S=2$ that enclosed our *entire galaxy* (i.e., a sphere of radius 50 000 light years) would undergo a homogeneous nucleation event somewhere within its vast extent only once every 20 million years! Even at $S=3$, a vapor sphere of radius 1 km exhibits formation of one supercritical embryo only once each half-hour, according to (23).

But, by virtue of the rapid reduction in height of the activation energy barrier with rising S, we find that raising S to 4 has reduced the waiting time to 0.2 sec for a system comprising only 1 cm^3 of vapor. This is getting us to the threshold of observable droplet formation in systems of laboratory size having commonly encountered sensitive times. But it is not until we go slightly above $S=4$ that we could count on seeing an observable concentration of drops in a chamber of typical order of sensitive-time (ten milliseconds) in the face of light-scattering problems that tend to make it doubtful whether droplet concentrations of less than 100 to 1000 cm^{-3} can be readily detected.[3]

Because it is in the very nature of nucleation that it is an irreversible process that need occur only once to "seed" an entire system, it may be well to point out that expansion cloud chambers actually present slightly different conditions than those assumed in Part I and most of Part II of this discussion. Nonadiabaticity of the chamber causes the temperature to rise and hence S to fall in a manner not related to droplet growth itself. In a sense, this peculiarity makes the unbalanced steady-state model with the Szilard boundary condition all the more realistic when applied to such chambers, for our entire concern in the cloud chamber problem is to get a moderate rate of production of supercritical embryos from a quasi-steady-state system in the time interval between the transient time of approach to the f_g distribution and the time of deterioration of adiabatic conditions due to conduction from the walls. (We do *not*, however, here permit action of the very ions whose heterogeneous nucleating effect is so indispensable in the most common application of expansion chambers in physics, so our model must not be misapplied to that case. See Mason[13] for a brief discussion of the role of ions as well as for extensive discussion of the type of heterogeneous nucleation important in cloud formation under natural conditions in the atmosphere.)

---

[13] See reference 3., p. 22.

VI. SUMMARY

By blending thermodynamic considerations discussed in Part I with kinetic considerations elaborated in Part II, students of homogeneous nucleation theory have obtained a relationship, Eq. (23), permitting rough prediction of the rate I at which supercritical embryos are formed per unit volume and per unit time in vapor supersaturated to any specified level S. The *thermodynamic* content of the theory provides quantitative specification of the opposing influence of surface-free-energy increases and bulk-free-energy decreases as fluctuation processes intermittently build up and destroy embryos of various sizes. The *kinetic* considerations interpret the same struggle in molecular-kinetic terms. Through use of a steady-state approximation to actual nucleation processes, and above all through use of the mathematical device of introducting the steady-state embryo population distribution function in writing Eq. (16), it becomes possible to derive the quantitative rate relation (23).

That Eq. (23) describes a nucleation rate I that really depends upon *fluctuation processes* in the vapor, tends to be rather well concealed in the simple specifications of the steady-state model employed, so it is well, in summary, to stress that the actual maintenance of the embryo population is a very lively affair describable only in terms of fluctuations, as embryos gain and lose molecules in rapid sequence. Those fluctuations, considered with reference to the state in which all the vapor molecules exist unattached, as monomers, quickly build up a statistically *nearly* steady population of clusters of molecules, or embryos, almost satisfying a distribution of the Boltzmann form, Eq. (4). The latter distribution is seen from Table II to be such that for, say $S=4$, $n^*=2\times10^{-8}$ cm^{-3}, whereas the actual number of embryos of nearly critical size, f_g^*, is even *less* than n^*. That such minute densities of the larger embryos serves for maintenance of a current of magnitude $I=5$ cm^{-3} sec^{-1} in vapor of that supersaturation, documents the lively, fluctuatory nature of the growth and decay processes involved. For to say that f_g^* is less than 2×10^{-8} cm^{-3} is equivalent to saying that embryos of that size have such transitory existence that one is present in a cubic centimeter of the vapor only about a billionth of the time. But despite this rarity, they do form and occasionally grow to size g^*—indeed, once every fifth of a second per cubic centimeter according to Table II. Then, if adverse probabilities do not quickly enter, these g^*-mers have a good chance of becoming supercritical and hence of growing *spontaneously*, both in the thermodynamic and the kinetic sense. Then, homogeneous nucleation has been achieved.

The theory summarized here would be very useful even if it did no more than call attention to the principal features of the thermodynamic and kinetic aspects of the peculiar process of homogeneous nucleation. However, experimental observations actually stand in tolerably good agreement with the predictions of the theory. As noted above, detectable production of droplets in laboratory-type expansion systems is predicted by (23) as requiring a value of S in the neighborhood of 5, and values ranging chiefly from about 4.5 to about 7 have been obtained in a variety of experiments.[3] When it is noted first that σ appears *cubed in an exponential* in our I-equation and second, that the possibility of still poorly understood size dependence of σ must be admitted, this degree of correspondence between theory and experiment should be regarded as indicating that (23) and the theory upon which it rests are probably fairly realistic description of the way in which real systems get over the free-energy activation barrier to phase transition.