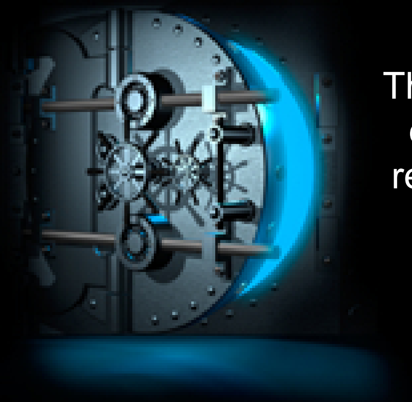

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ONR FOIA 18-021
March 23, 2018

Mr. John Greenewald Jr.
The Black Vault
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Castaic, CA 91384

Dear Mr. Greenewald:

This is the final response to your Freedom of Information Act (FOIA) request referred by the Defense Technical Information Center (DOD DTIC) and received by the Office of Naval Research on February13, 2018. This referral was given the number 18-021 in our system. You requested a copy of AD0404132 entitled "(U) Homogeneous Nucleation of Vapor Condensation. 1) Thermodynamic Aspects, 2) Kinetic Aspects." A copy of this documentation is attached. A copy of your request is also included with this letter for your reference.

If you have questions about this letter, please feel free to contact Mrs. Shanee Atwater at (703) 696-5361 or ONRFOIA@navy.mil. Please reference ONR FOIA 18-021 in any correspondence discussing this case.

Sincerely,

EDWARD ORLOWSKY
Director
Management Services Division

Attachments:
As stated

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Homogeneous Nucleation of Vapor Condensation. I. Thermodynamic Aspects

Homogeneous Nucleation of Vapor Condensation. II. Kinetic Aspects

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Homogeneous Nucleation of Vapor Condensation. I. Thermodynamic Aspects*

⑩ Org

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(Received February 2, 1962)

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In absence of all foreign materials or wall surfaces, phase transitions of the type vapor-to-liquid or liquid-to-solid are blocked by an activation-free-energy barrier. The latter arises from surface-free energy increases resulting from appearance of embryos of the more condensed phase. The thermodynamics of this type of phase transition are examined in Part I for the particular case of vapor condensation, a case for which theory and experiment now stand in tolerably good agreement. In Part II, kinetic aspects are ~~will be~~ considered.

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1. INTRODUCTION

IT is probably rather widely believed that if air containing water vapor, say on a humid summer day, is cooled to its dew point, droplets of water are certain to form by condensation. Similarly, it is fairly generally thought that if water is cooled to 0°C, freezing of ice is assured. Now although common experience does support both views, these views are incorrect if taken as generalizations applicable under *all* conditions. They become incorrect in those situations where vapors or liquids are cooled under conditions of uncommon purity, characterized by complete absence of foreign materials or wall surfaces which can render subtly important assistance to molecules seeking to condense or to solidify in well-behaved manner. Given completely pure vapor or liquid free from such extraneous influences we find that substances behave under cooling as if condensation point and freezing point simply did not exist—i. e., the pure phases exhibit, respectively, the phenomena of *supersaturation* and *supercooling*. The latter phenomena play important roles in many industrial processes and crop up in a wide variety of problems of basic scientific significance.

From both a theoretical and a practical point of view, one's insight into the mechanism of the everyday mode of "well-behaved" condensation and freezing is greatly enhanced by an understanding of the thermodynamic and kinetic principles of the "anomalies" of supersaturation and supercooling. Indeed, once one appreciates the latter principles, he clearly recognizes that the truly anomalous case is really that of the familiar behavior of condensation at the vapor's dew point or solidification at the liquid's freezing point!

It is the objective of the following discussion to present a summary of the general principles of nucleation of phase transition, using vapor condensation as the example. Because the kinetic theory of gases is well developed, whereas the kinetic theory of liquids is not, it becomes possible to describe rather more thoroughly the nucleation mechanism for condensation of vapor than for solidification from the melt. However, the general principles are quite similar in these two important types of phase transition, so the implications will be broad. In Part I of this discussion, chief emphasis is placed upon *thermodynamic* aspects. Part II will subsequently summarize the main features of the *kinetics* of nucleation processes. Emphasis throughout will be placed upon physical interpretation of the basic mathematical description of nucleation theory.

As a point of terminology, it may be noted that the type of nucleation to be considered here is referred to as *homogeneous nucleation* because it takes place in a completely homogeneous phase with no foreign bodies (ions, hygroscopic condensation nuclei, wall surfaces) present. When any of the latter are present and act to assist the system to get over the activation barrier which we shall see is imposed by surface-free-energy considerations, the process is properly called "heterogeneous nucleation." Systems of the inevitable degree of contamination accompanying almost all but scrupulously arranged laboratory experiments afford only examples of *heterogeneous nucleation*. It is our excessive familiarity with the superficial features of such ordinary heterogeneous nucleation processes that

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* Supported in part by the U. S. Office of Naval Research.

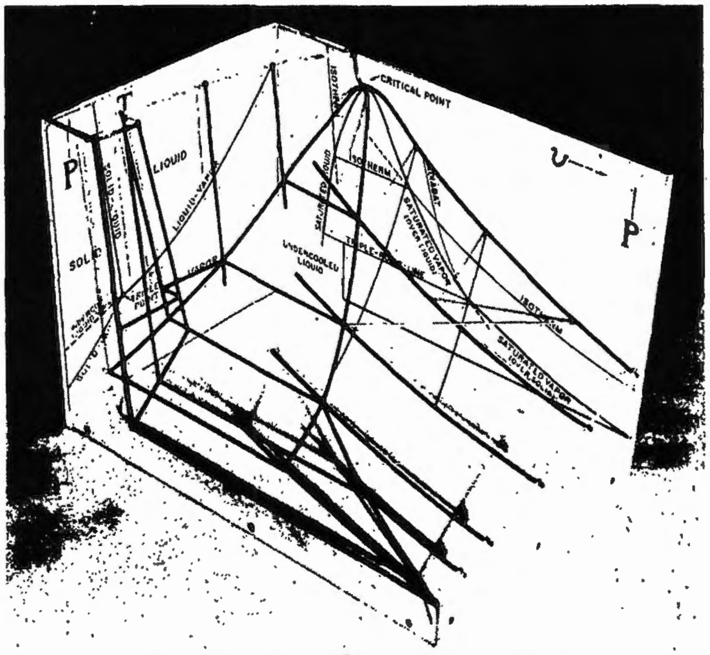

FIG. 1. Wire model of p-v-T surface for a substance such as water. Note metastable extensions of all ideal-vapor isotherms. In absence of heterogeneous nucleation, the system's characteristic point moves smoothly past the saturated vapor locus up along these metastable extensions as pressure is raised isothermally, starting from an ideal vapor state.

stands in the way of clear recognition of the nature of the conceptually more simple and more fundamental homogeneous nucleation processes which will be our main concern in the remainder of this discussion.

The ground work of the theory of nucleation of phase transition might be said to have been laid by Gibbs but the theory was not put into any very specific form until about the third and fourth decades of the present century, notably by Becker and Doering, Farkas, Volmer, Zeldovitch, and others. A fairly detailed, but not uniformly clear treatment of principles is presented by Frenkel.[1] Mason[2] presents almost verbatim a recent modification of Zeldovitch's analysis due to Farley, and gives a good critical discussion of the present state of experimental verification of the theory. A recent publication of the Faraday Society[3] should provide the interested reader with extensive bibliographical references plus several excellent summaries by such workers as Dunning, Mason, Fletcher, and others.

2. FREE ENERGY OF EMBRYO FORMATION

We may bring vapor to a supersaturated state of given temperature T and vapor pressure p (where $p>p'$, p' being the saturation vapor pressure of the substance in question at T) along a variety of paths, of which an isothermal compression path represents one very simple example. As we compress a vapor isothermally, we eventually reach its nominal condensation pressure, i.e., the saturation vapor pressure $p'(T)$ of the liquid phase of the same substance. Elementary discussions typically assert that further attempts to compress the system lead only to formation of steadily increasing amounts of the liquid phase, the characteristic point of the system merely sliding along an isobar-isotherm on the liquid-vapor region of the substance's equilibrium surface. This elementary viewpoint sidesteps the nucleation problem and can be considered correct only if foreign nuclei or wettable walls are assumed present to induce condensation at p'. In the absence of those latter heterogeneous nucleating agencies, the character-

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[1] J. Frenkel, *Kinetic Theory of Liquids* (Dover Publications, New York, 1955), pp. 366 ff.

[2] B. J. Mason, *Physics of Clouds* (Oxford University Press, New York, 1957), pp. 2–11.

[3] Faraday Society, *The Physical Chemistry of Aerosols* (Aberdeen University Press; Faraday Society Discussions No. 30, Aberdeen, 1960), pp. 9–45.

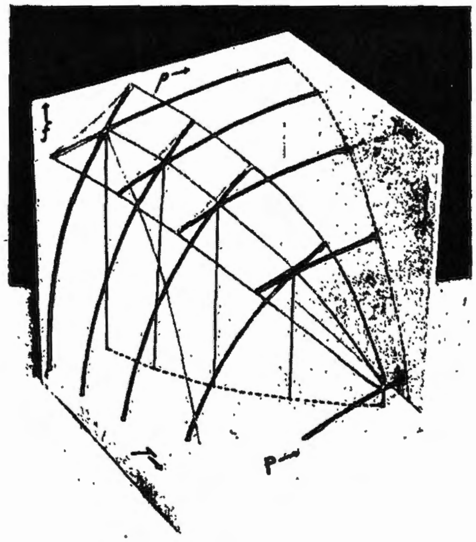

FIG. 2. Wire model of the Gibbs free-energy surface (f-p-T surface) for a pure substance, showing metastable extensions of isotherms and unstable segments of complete van der Waal's isotherms on upper leaf.

istic point of the system merely continues to move up along the *metastable extension* of the ideal-vapor isotherm on which it approached point p', T.

This is illustrated on a three-dimensional wire model of an equilibrium p-v-T surface, designed by the writer for use in classroom discussions of nucleation thermodynamics and shown in Fig. 1. A few representative wire isotherms are shown in the vapor region, and short extensions into the supersaturated vapor region can be seen to represent the metastable supersaturated states attained by isothermal compressions. (This model was designed to illustrate a number of other important thermodynamic principles and processes beyond the scope of this discussion. The writer would point out that such wire models prove more considerably useful in classroom use than molded surfaces of the type commercially available.)

Now as our system's characteristic point moves up the metastable extension of its ideal-vapor isotherm, its specific Gibbs free-energy f (dimensions ergs g^{-1}) rises above that for the liquid phase at the same temperature T. The differential relation $df=vdp-sdT$, where v and s are, respectively, the specific volume and specific entropy of the vapor, may be integrated along the metastable isotherm from saturation pressure p' to some supersaturated pressure p, giving as the *excess* of f over that for liquid at the same temperature T familiar expression

$$\Delta f = RT\ln(p/p'), \qquad (1)$$

where R is the gas constant per gram of the vapor in question. We assume p to be well below the substance's critical pressure, so that the ideal gas law holds. It must be stressed that at the moment we assume *no* appearance of embryonic droplets in our supersaturated vapor. As we shall see below, this is an unrealistic assumption but one that is conceptually useful for the moment.

For any pure substance, it is possible to construct a three-dimensional f-p-T surface. Enlightening discussion of the general form and principal properties of such a surface have been given by Callen,[4] and by Pippard,[5] and from their treatments the writer drew the idea of constructing the wire model shown in Fig. 2. No numbers are entered on the axes since this model is only a qualitative representation. It shows vapor-region isotherms rising steeply (large specific volume) to the locus of intersection with the liquid-region isotherms which have much lower slope, in accordance with the derivative properties of the relation $df=vdp-sdT$. The model suggests the greater *negative* slope (large specific entropy) of the isobars in the vapor as contrasted with the liquid region. But most significantly for the present discussion, the model shows the extensions of all the vapor isotherms that overlie the liquid region near the locus of saturation. (The latter locus is the midrib of the leaf-shaped "surface" extending diagonally across the top of the model. Note that this skew curve has as its projection on the p-T plane the familiar saturation vapor pressure curve, shown in the model as a dotted curve. The verticals are merely supports, though they aid in revealing the preceding projective relationship.) That these extensions, counterparts of those in the p-v-T model of Fig. 1, *overlie* the

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[4] H. B. Callen, *Thermodynamics* (John Wiley & Sons, Inc., New York, 1960), pp. 146–163.

[5] A. B. Pippard, *Classical Thermodynamics* (Cambridge University Press, New York, 1960), pp. 116–121.

liquid region, is consistent with the metastable nature of the associated supersaturated states, for the vapor there has a finite excess of free-energy over that of the liquid at the same temperature. (The cuspate junctions of these metastable extensions and the crossribs on the upper part of the model in Fig. 2 are related to the van der Waals' equation of state, but will not be discussed here. Their significance is best appreciated by consulting Callen's or Pippard's treatments of this type of surface.)

Since it is the spontaneous tendency of thermodynamic systems to assume a state of lowest possible Gibbs free-energy, we must now ask why a system whose characteristic point is somewhere on the metastable supersaturated vapor portions of the surfaces modeled in Fig. 1 and Fig. 2 does not simply jump to the available state of lower f in which newly formed liquid phase is present in equilibrium with the residual vapor. The answer is this: The only possible route to the state of smaller f is *via dropwise condensation* (assuming no foreign nucleants and remoteness of containing walls or else completely nonwettable walls); and as soon as embryonic droplets enter the picture we must reckon with the *surface-free-energy* of the interfaces between the drops and the surrounding vapor. When a bit of vapor condenses, the *decrease* in free-energy due to condensation (bulk-free-energy change of phase transition) varies as the mass condensed, i.e., as the *volume* of liquid droplet formed, while the surface-free-energy *increase* varies as the *area* of the droplet. If r is the droplet radius, the positive term varies as r^2, the opposing negative term as r^3, and regardless of the magnitudes of the coefficients of these terms, the positive r^2 term is mathematically certain to dominate over the r^3 term in *some* sufficiently small r interval above zero. Therein lies the obstacle to attaining the stable state of lower f depicted in Fig. 2. That preferred state lies a finite distance away and may only be reached by a path that crosses the "forbidden region" in which the *increases* in f due to appearance of new surface energy dominate over bulk-free-energy *decreases* in f.

We can describe this mathematically by now taking as a more convenient f-reference state that in which we initially have supersaturated vapor at some given high vapor pressure $p(p>p')$ at temperature T, and in which it is assumed that not a single embryonic droplet exists. The latter proviso, it must be carefully noted, is to be construed as ruling out dimers, trimers, and all other clusters of molecules, however small. Then the rise ΔF in the free-energy of our system as we isothermally and (essentially) isobarically form a spherical embryo of some small radius r can be written as

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

The first term on the right is the intrinsically positive contribution of the surface-free energy, where σ is the specific surface-free-energy having dimensions ergs cm^{-2}. (In liquids, σ is also the familiar surface tension; in the case of the solid-liquid interfaces arising in nucleation from the melt "surface tension" loses meaning, but remains well-defined as the specific surface-free-energy.) The second term, in which ρ is the liquid density and $S=p/p'$ is the vapor supersaturation ratio, represents the contribution to ΔF made by the bulk-free-energy change.[6] Its form is taken from (1), but the sign is reversed, of course, because of our new choice of reference state. The bulk-free-energy change in going from vapor at p', T to liquid inside the drop formally comprises *three* parts. The *first* is that obtained in isothermally lowering the vapor pressure from p to p'. The *second* is obtained in condensing vapor at p', T to liquid at p', T, and is *zero* by the equilibrium property of f. The *third* is obtained in isothermally compressing the *liquid* from pressure p' to the high internal pressure of the liquid within the droplet of radius r, but can be shown to be a numerically quite small contribution in view of the small specific volume of the liquid. (There are alternative ways of formulating the over-all problem here which ignore surface-free-energies as such and instead deal explicitly with the effects of high internal pressure on the free-energy of the droplet. These can be shown to be fully equivalent albeit seemingly dissimilar thermodynamic routes to the same goal.[7]) Of these three contributions, only the first is important and is written as the right-hand member of (2).

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[6] The reader should note carefully that S will, throughout this paper, denote the vapor supersaturation ratio p/p', and not the entropy, for which the same symbol is often used.

[7] J. Frenkel, see reference 1, p. 369.

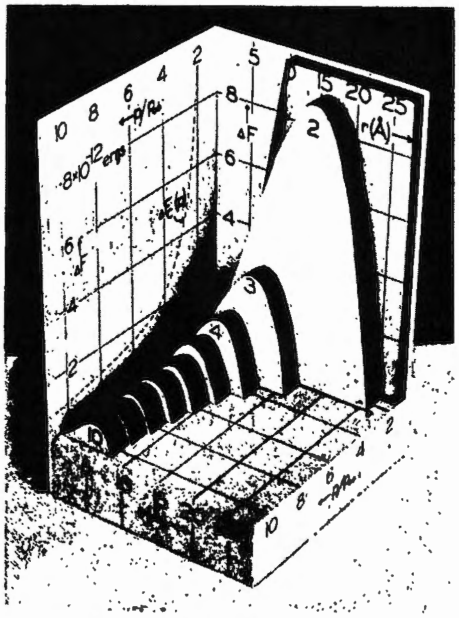

Fig. 3. Wood and plastic model of ΔF-S-r surface for water vapor at 0°C.

Equation (2) specifies ΔF as a function of r and S for fixed T, whence it follows that one may construct a ΔF surface over the r-S plane. A *quantitatively* accurate model of such a ΔF-r-S surface is shown in Fig. 3, calculated for the case of water vapor at 0°C. It displays many thermodynamic features of importance in homogeneous nucleation theory. Note from (2) that for the limiting case $S=1$, the bulk term vanishes and ΔF rises monotonically as a parabola, depicted in the model of Fig. 3 by the transparent plastic lamina in the $S=1$ plane (p' is identified on the model as p_∞, denoting infinite radius of curvature of the liquid surface, the condition tacitly assumed to hold in the customary definition of saturation vapor pressure p'). For *subsaturated* vapors, the ΔF curve would rise even more steeply, because a *fractional* S makes the second term on the right go *positive*, reinforcing the effect due to the surface-free-energy barrier, a thermodynamically quite understandable situation.

For $S>1$, however, the second term is a *negative* contribution to ΔF, its magnitude rising as the degree of supersaturation is raised. Its presence assures existence of a maximum in ΔF at some r, the value of the latter falling as S rises. This very important feature of (2) is depicted in the model of Fig. 3 by the calculated profiles of the wood laminae inserted for integrally rising values of S ranging from 2 up to 10. As we shall note in the next section, *the presence of these maxima is fundamentally significant in nucleation theory*. They represent the summits of the free-energy activation barriers blocking the formation of the new phase, and can only be surmounted as a result of rare fluctuation phenomena in the supersaturated vapor.

It is illuminating to consider somewhat further the cases where $S\leq 1$. Even though such thermodynamically stable cases do not enter directly into phase transition nucleation processes, some of their characteristics shed important light on our problem. Contrary to the ordinary point of view, subsaturated or just-saturated vapor is not completely free of embryos of the liquid phase (nor is supercooled liquid completely free of embryos of the solid phase). Rather, there exists a *statistically steady-state population of embryos* characterized by the Boltzmann-like distribution function

$$n_g = n_1 e^{-\Delta F/kT}, \tag{3}$$

where now we use the number of molecules g per embryo rather than r as the size parameter of the embryo; n_g is the number per unit volume of vapor of embryos of size g, k being the Boltzmann constant.[8] Here ΔF is, by (2), a rapidly increasing function of r (and hence also of g) because the second term on the right in (2) is nonnegative when $S\leq 1$. Illustrative values of n_g computed from the distribution Eq. (3) for water vapor at 0°C with saturation ratios $S=0.5$ and $S=1$ and for three values of g are given in Table I. One cubic centimeter of half-saturated

Table I. Values of n_g (cm^{-3}) for two saturation ratios S.

$g\rightarrow$	5	10	20
$S=0.5$	1×10^{4}	5×10^{-5}	6×10^{-18}
$S=1.0$	3×10^{5}	5×10^{-2}	6×10^{-12}

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[8] J. Frenkel, see reference 1, p. 380, gives a lengthy proof of Eq. (3); the present writer knows of no simple proof for existence of such a Boltzmann-type distribution of embryos. To express ΔF in terms of g and not r, one uses the relation $(4/3)\pi r^3\rho = gm$, where ρ is the density of the liquid phase and m is the mass of one molecule.

water vapor at 0°C is seen to contain the surprisingly large number of ten thousand 5-mers at any instant, some destined momentarily to fly apart, others to be joined by a third to contribute in the next moment to the instantaneous 6-mer population. The concentration of clusters of larger g falls sharply according to (3), and for $S=0.5$ and $g=20$ is already down to about 10^{-17} cm^{-3}. For just-saturated vapor all the n_g are larger, of course, and Table I shows that even 10-mers, embryos that have been built up by a fortuitous concatenation of collisions to an aggregate of ten water molecules, are present at $S=1$ in mean concentration as high as 0.05 cm^{-3}, i.e., an average density of about 1 in every 20 cm^3 of saturated vapor.

However, 10-mers lie well on the low side of the maxima of the ΔF curves (Fig. 3) even for moderate degrees of supersaturation, so their fluctuatory presence in just-saturated vapor by no means provides the necessary path for the system to begin its condensational phase transition to stabilize itself in the face of further compression. Equation (3) predicts still more infrequent occurrence of embryos of size beyond the limit of 20 displayed in Table I. Thus, one finds that a cube of just-saturated vapor some 2.3 miles on edge would, on the average, contain just *one* embryo of size $g=25$, and Eq. (3) shows that one would not find a single cluster of size $g=50$ at a randomly chosen instant unless he had a cube of vapor ten million miles on edge! Trading time for volume, one thus senses that with vapor samples of moderate size (say, cloud-chamber size), he would have to wait for centuries on end before witnessing the chance build-up of an evanescent aggregate containing even only a few tens of molecules in his sample if $S=1$. This is another way of viewing the practically insuperable barrier to phase transition at $S=1$ in absence of heterogeneous nucleants such as ions or wettable surfaces.

In computing values of n_g for Table I, a tacit assumption conventionally made in nucleation theory has been employed, namely that we may proceed without too serious error, to assume that the bulk value of σ continues to have meaning even down to quite small molecular aggregates. This assumption has been discussed from a variety of viewpoints in recent years, summaries of which will be found, for example, in Davies and Rideal.[9] Briefly, weight of argument indicates that we may use bulk values of σ with fair accuracy down to values of g of order 10–20 but below that the effective value of σ probably diminishes and we should resort to some direct molecular-bond calculation. This limitation must be kept in mind in assessing all results for very small g. The above-estimated 5-mer concentration, for example, must be regarded as good to order of magnitude at best.

3. CRITICAL EMBRYOS AND THE KELVIN EQUATION

In discussing Eq. (2) and the model shown in Fig. 3, we have noted that ΔF exhibits a maximum for any case for which $S>1$. Invoking the basic rule that any process in which F *decreases* is a spontaneous process, we see that if, by any means, our system can get up to the summit of its particular ΔF curve, the slightest additional condensational growth of the droplet beyond the size associated with that summit should lead to irreversible growth of the drop at the expense of the supersaturated vapor, and the characteristic point will plunge rapidly down the right-hand portion of the ΔF-r curve (Fig. 3). That is, the r for which ΔF attains its maximum will be a *critical embryo radius* for whatever S we are dealing with.

To determine this critical radius r^*, we differentiate both sides of (2) partially with respect to r holding T and S constant (remembering that while the droplet is as tiny as a subcritical embryo in, say, a cubic centimeter of vapor, its growth will not deplete the vapor stock by an amount producing measurable change in p, nor will its latent heat-release sensibly alter T). On setting the derivative equal to zero and solving for the thereby specified critical radius we find

$$r^*=2\sigma/\rho RT(\ln S). \qquad (4)$$

This relation reveals the very important rule that *the larger the supersaturation ratio S, the smaller the critical radius r**. In Table II the sizes of the critical embryos corresponding to several values of $S>1$ are indicated, expressed in terms of numbers of molecules as well as in

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[9] J. T. Davies and E. K. Rideal, *Interfacial Phenomena* (Academic Press Inc., New York, 1961), p. 11.

TABLE II. Radius r^* and number of molecules g^* per critical embryo for various supersaturation ratios S.

S	2	3	4	5	6	7	8
r^* (Å)	17.0	10.7	8.5	7.3	6.6	6.0	5.7
g^*	695	174	87	55	40	31	26

terms of r^* directly. Noting from Table II that g^* is still as large as several hundred molecules even when we raise S beyond 2 (200% relative humidity if we return momentarily to the meteorological context), we see again how impossible it is to find critical embryos present unless S is quite high, the fundamental lesson learned from thermodynamic analysis of the nucleation problem.

Note that Eq. (4) is just Kelvin's equation for the enhanced saturation vapor pressure over a surface of small radius of curvature, now however appearing as the equation for the critical radius corresponding to a given supersaturated vapor pressure. These two seemingly different interpretations of (4) are not really distinct: In order that an embryo of radius r^* may be in metastable equilibrium with the surrounding vapor, it clearly must have just such a curvature as to raise its effective saturation vapor pressure from the value $p'(t)$ to the pressure p of the surrounding supersaturated vapor. Of the two interpretations, the critical-radius interpretation is much the more meaningful here, of course.

If we differentiate (2) a second time and examine the resulting sign, we find the second derivative to be intrinsically negative for $S>1$, confirming that our stationary value at r^* is, as depicted in Fig. 3, a *maximum*. Guggenheim gives what seems to this writer to be the most carefully and broadly formulated definition of a *metastable state*: any state which is stable with respect to *all* states differing only infinitesimally from the given state, but unstable compared with *some* other state differing finitely from the given state. The state associated with the maximum of the ΔF curve for any given value of S is thus, by Guggenheim's criterion, a metastable state. Curiously enough, we deal here with *a metastable state built, as it were, upon another metastable state*; for the supersaturated vapor itself exists in a metastable state before the beginning of formation of the critical embryo that is itself metastable with reference to the supersaturated vapor!

If we substitute the value of r^* from (4) back into the general equation (2) for ΔF, we evaluate the height of the free-energy activation barrier as

$$\Delta F^* = 16\pi\sigma^3/\{3(\rho RT\ln S)^2\} = 4\pi r^{*2}\sigma/3. \quad (5)$$

In (5) ΔF^* is written in two equivalent forms, of which the latter, interpreted as one-third the product of the area of the critical embryo multiplied into the specific surface-free-energy can be carried over to nucleation of solids and used even in the event that the embryo must be assumed nonspherical for crystal-habit reasons. Gibbs used this latter form in his analyses, whence that form is sometimes identified as the Gibbs relation. Note that S enters (5) in such a way as to cause ΔF^* to fall off rapidly with rising S, at the same time that (4) shows r^* also diminishing with rising S. Equations (4) and (5) convey the fundamental thermodynamic moral of nucleation theory: *Raising the degree of supersaturation markedly enhances the probability that fluctuation processes will send some embryo over the top of the activation barrier in a given time because raising S reduces the embryo size r^* and the associated height ΔF^* of the top of the barrier.* Figure 3 displays this important point quite clearly. On the F-S plane of that model the projection of the skew curve passing through all the barrier summits has been plotted as the dashed curve (there labeled "ΔF_c", with c for "critical") that falls rapidly as the supersaturation ratio increases.

As will be elaborated in Part II of this discussion, a further enhancement of nucleation probability results from increasing S—namely the obvious effect of increased molecular bombardment rate attending any rise of vapor pressure. But this latter effect will be shown to be far less important than that cited in the preceding paragraph.

We may summarize all that has now been said: Sufficient increase of S (as we shall find, to values somewhere in the neighborhood of *five*) finally serves to raise the molecular bombardment rate and to reduce r^* and the attendant height of the activation energy barrier ΔF^* to such extent that the probability of some subcritical embryo fortuitously growing to supercritical size in a short time approaches unity. At that S value, homogeneous nucleation becomes an effective process, and phase transition can finally begin.

From the above statements it is clear that nucleation is ***intrinsically a probabilistic event.*** We may speak of the probable rate of appearance of critical embryos in a given volume of vapor at given S, or more meaningfully, we may speak of the average time we must wait for a single nucleation event in our given volume of vapor at supersaturation ratio S. The latter is the more physically realistic way to view the matter, inasmuch as it is generally true that once a *single* nucleation event has occurred ***anywhere*** within our system, it suffices to stabilize the *entire* system. In Part II we shall, however, find it mathematically more convenient to ask for the rate of appearance of nuclei under certain steady-state conditions contrived to simulate rather well the actual conditions preceding appearance of that first, crucial nucleus in our system.

Homogeneous Nucleation of Vapor Condensation. II. Kinetic Aspects*

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(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

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

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

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

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

$$r^* = 2\sigma / \rho RT \ln S. \tag{3}$$

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).

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* 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

$$C = 4\pi r^2 q p/(2\pi m k T)^{\frac{1}{2}}, \tag{5}$$

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

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[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 1, 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.

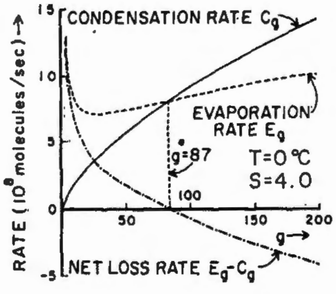

FIG. 1. Variation of condensation and evaporation rates with embryo size g. Case shown is for water vapor at 0°C, $S=4.0$.

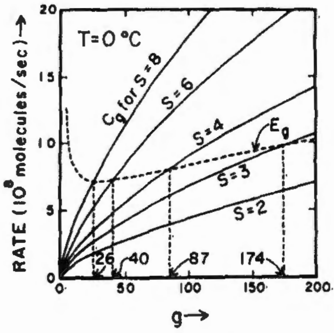

FIG. 2. Effect on g^* due to varying S at fixed T.

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

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[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[8] 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.

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,

$$C_g n_g = EC_{g+1} n_{g+1}. \qquad (10)$$

Defining the ratio of the populations of neighboring g states as

$$J_g = n_g / n_{g+1} \qquad (11)$$

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

$$J_g = S^{-1}\exp[(A/kT)\{(g+1)^{2/3} - g^{2/3}\}]$$
$$\approx S^{-1}\exp[2A/3kTg^{1/3}], \qquad (12)$$

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.

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

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,

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

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,

$$f_G \equiv 0. \qquad (14)$$

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

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[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

$$\lim_{g\to 1}(f_g/n_g)=1, \tag{15}$$

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

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

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

$$\begin{aligned} I/C_1 n_1 &= f_1/n_1 - f_2 n_2 \\ I/C_2 n_2 &= f_2/n_2 - f_3/n_3 \\ &\ \vdots \qquad\qquad \vdots \\ I/C_{G-2} n_{G-2} &= f_{G-2}/n_{G-2} - f_{G-1}/n_{G-1} \\ I/C_{G-1} n_{G-1} &= f_{G-1}/n_{G-1} \end{aligned}$$

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

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

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 $1/C_g n_g$. 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

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[9] Here it is quite important to keep in mind that nucleation is actually accomplished by values of I (units of cm^{-3} 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.

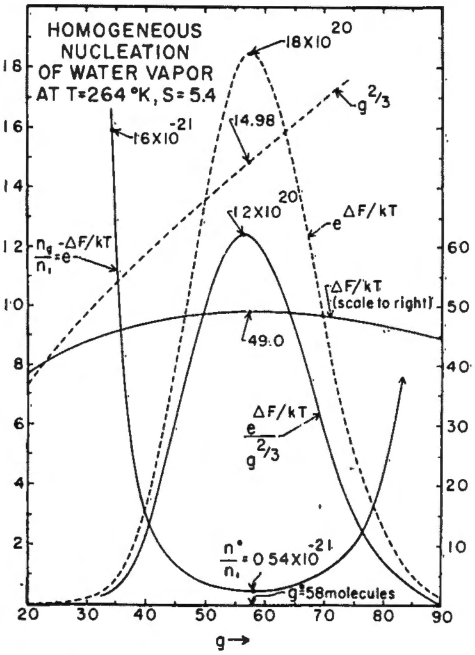

FIG. 3. Behavior of nucleation parameters in the critical region. Data refer to water vapor at 264°K, $S=5.4$, corresponding to experimental case studied by Barnard (see Mason[3]).

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,

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

(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 $g^{2/3}$, 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.,

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

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

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

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

With these approximations (18) becomes, on

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[11] See reference 3, p. 17.

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

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

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

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

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

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

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

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[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(cm^{-3} sec^{-1})	4×10^{-83}	2×10^{-17}	5	2×10^{7}	3×10^{11}	1×10^{13}	4×10^{16}
n^*(cm^{-3})	3×10^{-81}	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_0 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_0 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[18] 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.)

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[18] 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_0^*, 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_0^* 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.