THE DYNAMICS
OF
CONDENSATION AND VAPORIZATION

Thesis by

Forrest Richard Gilmore

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1951

ACKNOWLEDGMENTS

The writer wishes to thank Professor M. S. Plesset for his invaluable help and encouragement during the course of this investigation.

ABSTRACT

The condensation process in supersaturated vapors is analyzed with the help of thermodynamics and kinetic theory. The simplifying approximations which make the problem tractable are carefully examined. Results are obtained for the steady rate of condensation which constitute a theoretical improvement over Becker and Döring's values. The uncertainties in the values of the free energy for very small droplets, which are only partially removed by Tolman's theory on the variation of surface tension with curvature, limit this improvement in the condensation theory.

Nonsteady condensation situations are also treated in detail by means of numerical and graphical integrations. It is found that the condensation in such situations generally approaches a steady rate in time periods of the order of 1 to 100 microseconds. Such time periods are negligible in many physical situations, but may be significant in the case of condensation shocks in wind tunnels.

A similar analysis is carried out for the boiling of superheated liquids and the rupture of liquids under tension. Approximations reduce the analysis of these processes to mathematical relations very similar to those for the condensation process. Nonsteady solutions are obtained by numerical integration. It is found that the solutions ordinarily approach a steady rate of bubble formation in less than a microsecond.

TABLE OF CONTENTS

I. INTRODUCTION

When a vapor is condensed to a liquid, or when a liquid is vaporized, the process frequently does not follow the simple scheme of a single mass of liquid and a single mass of vapor, one of which steadily grows at the expense of the other. Instead, droplets or bubbles, which are embryos of one phase dispersed in the other, are commonly formed. These embryos greatly complicate the process, not only from a mechanical standpoint, but also from a thermodynamic one, since the small embryos have "surface" energies and entropies comparable with their "volume" energies and entropies. It is essentially these surface effects which permit the existence of metastable states such as supersaturated vapors and superheated liquids.

An adequate theory of the dynamics of this phase transition would contribute to many fields of science and technology. It should be applicable, for example, to the condensation of droplets in atmospheric clouds and in Wilson cloud chambers, to condensation shocks in supersonic wind tunnels, to cavitation in pumps and on marine propellers, and to many types of boiling problems.

An attempt at such a theory, based on thermodynamics and gas kinetics, was made by Volmer and Weber,[1, 2] and improved by Farkas,[3] Kaischew and Stranski,[4] and finally by Becker and Döring[5, 6] and Zeldovich.[7, 8] A somewhat different development, based on the theory of absolute reaction rates, has recently been given by Turnbull and Fisher.[9, 10] All of these investigators make a number of approximations and simplifying assumptions, the validity of some of which is very difficult to determine. Moreover, some of their results apparently disagree with experiment, especially in the cases of vapor condensation shocks and liquid tensile strengths. (It should be emphasized, however, that in this field the experimental measurements frequently do not agree with each other.)

The aim of the present work has been to remove some of the approximations made by previous investigators and to estimate the accuracy of the remaining ones. In the more generalized treatment presented here, the Becker-Döring theory becomes a special case.

II. THEORY OF CONDENSATION (DROPLET FORMATION)

Although the theory of condensation and the theory of vaporization to be developed in this paper are quite similar, the significance of the approximations introduced is much more obvious in the condensation case; therefore, condensation will be studied first.

2.1. Preliminary Considerations

When a pure vapor is brought from an undersaturated or saturated state to a sufficiently supersaturated state (by adiabatic expansion, for example), the vapor condenses into liquid droplets. These droplets have presumably been formed by a chain process which starts with the association of two molecules to form a two-molecule aggregate; this aggregate or "droplet" captures a third molecule, then a fourth, and so on. The mean growth rate of a given droplet will be decreased or perhaps even made negative by the frequent escape (evaporation) of molecules. The occasional consolidation of two polymolecular droplets, or the converse fission process, may affect over-all condensation significantly. Moreover, as first shown by Frenkel,[11, 12] vapors in the saturated or nearly saturated state contain, in equilibrium, appreciable numbers of droplets consisting of from two to about ten molecules; these naturally serve as nuclei for the growth of larger droplets.

A supersaturated vapor is, by definition, thermodynamically unstable with respect to spherical masses of liquid large enough so that their surface curvature may be neglected; these very large "droplets" will grow at the expense of the vapor molecules. Smaller droplets, however, are less stable than large droplets, essentially because of their greater proportion of loosely-bound "surface molecules" compared to the more tightly bound interior molecules. Thus, as smaller and smaller droplets are considered, a size will be found which is in approximate equilibrium with vapor molecules of a given degree of supersaturation. This size is called the "critical size;" analytical expressions for it will be derived later, but generally it corresponds to droplets containing on the order of 10 to 200 molecules, for supersaturation ratios of physical interest. The equilibrium between the vapor molecules and the critical droplet is an unstable equilibrium, because a critical droplet which happens to lose a molecule becomes less stable and thus will (on the average) rapidly lose more molecules until it is completely vaporized, while, conversely, if it gains one molecule it will grow at an accelerating rate. The growth of any particular sub-critical droplet up to critical size is therefore an improbable process occurring through fluctuations from the average behavior of sub-critical droplets. An individual droplet grows or shrinks in finite jumps by a stochastic process, and there exists a certain small probability that it will attain or exceed critical size. Most condensation situations of physical interest involve a very large number of vapor molecules; a significant number of droplets of critical size may be formed from these molecules even though the probability for any given molecule to initiate the growth be very small. Droplets which grow beyond critical size are increasingly likely to continue to grow, and a droplet which has reached about twice the critical size is virtually certain to attain macroscopic size.

A question which arises before the condensation process can be treated mathematically is whether the vapor-droplet mixture can be regarded as "homogeneous," or whether significant density and temperature gradients will occur in the vapor immediately surrounding each growing droplet. In a typical case of water vapor at 0° C and four times the saturation pressure, a spherical volume of radius equal to the mean free path of the vapor molecules contains about 10^7 molecules, and similarly large values are obtained for other vapors and conditions of interest.* Thus any depletion of the vapor in the neighborhood of a droplet growing up to 10^5 molecules, say, would be equalized in a time short compared to the droplet growth time, and also any heat conducted away from the droplet by escaping molecules will be spread over a region containing many more molecules in a similarly short time. It follows that homogeneity in the vapor can be safely assumed until the droplets grow to many times critical size. Beyond this point, density and temperature gradients in the vapor may have to be considered; but, on the other hand, for such "large" droplets the actual irregular molecule-by-molecule growth process can be

---

*If the molecular diameter is estimated from the volume occupied by a molecule in the liquid state, it is easily shown in general that the number discussed above equals $(\sqrt{2}/108)\,(\rho_L/\rho_V)^2$, where ρ_L and ρ_V are the densities of the liquid and vapor, respectively.

accurately approximated by a continuous steady growth, so that the problem is still mathematically tractable. Thus, it is convenient to separate the complete condensation process into an early "molecular domain" and a later "macroscopic domain" with the dividing point taken at droplets containing about 10^4 or 10^5 molecules. Fortunately, in the transition region all of the approximations pertinent to either domain should be valid, so that the exact choice of the dividing point is immaterial.

In treating the condensation process, one might try to follow the growth history of particular droplets, or alternatively, one might examine the change with time of the populations of the various size-groups. These alternatives correspond to the use of "Lagrangian" or "Eulerian" coordinates, respectively. In the molecular domain, Lagrangian coordinates yield complicated stochastic equations, since the growth of a molecular-sized droplet is a very erratic process, while Eulerian coordinates yield considerably simpler equations, corresponding to a "generalized diffusion" process. Hence, Eulerian coordinates will be used in the present work (except in Appendix 3; see section 2. 2).

In the macroscopic domain, on the other hand, it proves simpler to use Lagrangian coordinates, since the growth of a single macroscopic droplet can be considered to be steady and continuous. The growth of macroscopic droplets has been studied by Hazen[13] and Barrett and Germain[14], who found that theoretical relations based on macroscopic diffusion and heat conduction give results in good agreement with experiment. This macroscopic domain will not be treated in the present paper.

2.2. Choice of Variables

To treat the condensation process mathematically, let us characterize any given aggregate or droplet by the following three independent parameters: n, the number of molecules it contains (with n = 1 representing the monomolecular vapor); E, the internal energy of the droplet; and η, the kinetic energy of motion of the center of mass of the droplets ($E + \eta$ = total energy). By thus limiting the characterization to these three parameters, we tacitly ignore any variations in size and shape between droplets having the same mass and energy, and any non-equilibrium distribution of the energy among the various parts of a droplet (i.e., "internal temperature gradients"). The first neglect appears reasonable because droplets containing a dozen or more molecules are virtually certain to be nearly spherical, to minimize the surface free-energy, while droplets containing fewer molecules can probably be approximated by a mean size and shape with an error not greater than the other errors which arise when extremely small droplets are treated. As will appear later, a considerable error in the treatment of droplets containing only a few molecules may affect the calculated condensation process only slightly. The neglect of internal temperature gradients is made plausible by arguments given in Appendix 1, from both a molecular and a macroscopic thermal-conductivity point of view. Even with these approximations, the general problem gives rise to differential equations in four independent variables: n, E, η , and t (the time).

The variable η can be eliminated by assuming that all droplets of a given size, n, have velocities (and kinetic energies) distributed according to Maxwell's law for a certain temperature, T, which will be called the "kinetic-energy temperature," and which is independent of n and E but may depend on time. This assumption appears fairly reasonable, since any assemblage of moving particles that undergo either completely elastic or completely inelastic (capture) collisions tends toward a Maxwellian velocity distribution (with the usual mass dependence), as shown in detail in Appendix 2, and condensation processes of interest usually take place over time periods long enough to permit each droplet to undergo many collisions.

The independent variables are thus reduced to three. The differential equations which arise, however, are still too complicated to be solved analytically or even by a conventional numerical method in a reasonable amount of time. The most feasible method appears to be the "Monte Carlo method" of actually tracing the histories of a large number of typical droplets. An outline of such a procedure for the condensation problem is presented in Appendix 3. Numerical results from such a procedure can be obtained only through extremely lengthy manual computations, or extensive use of automatic computing machines, neither of which has been possible in the present work. Such computations are planned for the near future.

In order to bring the problem into more tractable form, two further approximations will be made. First, the droplets will be treated as if at any instant all the droplets of a given size, n, have the same free energy, F_n, which may be a function of n and t. This neglect of the free-energy dispersion is equivalent to the neglect of the internal-energy dispersion, since, under the approximations made, the one quantity is a monotonic function of the other. Each free-energy value, F_n, also corresponds to a certain temperature, T_n, for droplets of size n. The second approximation which will be made is that $T_n = T$ for all values of n. This assumption undoubtedly introduces some error, since the growing droplets in general will have higher temperatures than the surrounding vapor, due to release of the latent heat on condensation. In cases where the vapor is mixed with a non-condensing gas, the error should be smaller, since the gas molecules will help carry away this heat. A discussion of the error introduced by this approximation will be given in a later section.

Actually, much of the theory presented below can be carried through for arbitrary $T_n(t)$, without assuming $T_n = T$. The difficulty is then to find an approximation to T_n better than T. A successful method for doing this has not yet been discovered. Even if the mean temperature for all the droplets of a given size, n, could be calculated, use of this value for the effective T_n in the condensation equations may introduce as great an error as use of T, since in general only a very small fraction of the submicroscopic droplets grow to observable size, and these are likely to be those which initially were much colder than the mean droplet temperature.

2.3. Kinetic Fundamentals

Let $N_n(t)$ $(n = 1, 2, 3, \ldots)$ be the number of n-molecule droplets per unit volume, in a mixture of vapor molecules and droplets of various sizes, all having velocity distributions corresponding to the kinetic-energy temperature T(t). Then the rate of collision of droplets containing i molecules with droplets containing j molecules is $2\,(2\pi kT/m)^{1/2}\,D_{ij}^2\,[(i+j)/ij]^{1/2}\,N_i N_j$ per unit volume, where k is Boltzmann's constant, m is the mass per molecule, and D_{ij} is the mean collision diameter.[12] If the droplets were perfectly spherical and had the same density, ρ_L, as the liquid in bulk, then D_{ij} would equal $(3m/4\pi\rho_L)^{1/3}\,(i^{1/3} + j^{1/3})$. By multiplying these quantities by a "correction factor," α_{ij}, one can take as the exact rate of capture collisions (not counting collisions which do not result in the two particles sticking together):

$$\text{Rate of } i + j \text{ capture collisions} = K T^{1/2} \alpha_{ij} (i^{1/3}+j^{1/3})^2 \left(\frac{i+j}{ij}\right)^{1/2} N_i N_j, \tag{1}$$

where the quantity K is given by

$$K = \left(\frac{2m}{\pi}\right)^{1/6} \left(\frac{3}{\rho_L}\right)^{2/3} k^{1/2} \tag{2}$$

and is constant for any particular liquid, if the variation of liquid density with temperature and pressure is neglected. The factor α_{ij} is introduced not only to allow for collisions which do not result in capture, but also to correct for any non-sphericity of the droplets or any deviation of the droplet density from ρ_L.

When $i = 1$ and $j \longrightarrow \infty$, the quantity α_{1j} becomes the conventional accommodation coefficient, α, for individual molecules striking a flat liquid surface. The best experimental evidence[2] indicates that for clean liquid surfaces at temperatures not greatly different from room temperature, α is probably very close to unity.

When j is small, α_{1j} can be considered to contain a geometrical factor slightly greater than unity due to non-sphericity of the aggregates and densities less than the liquid in bulk, and a factor somewhat less than unity because of collisions which do not result in capture. For very small and simple "droplets," such as aggregates of 2 or 3 monatomic molecules, the latter factor may be several orders of magnitude smaller than unity, because of the inability of the limited number of degrees of freedom of the aggregate to absorb the collision energy rapidly. However, for polyatomic molecules it is believed that α_{1j} is near unity even for values of j as small as 3 or 4.

Similar considerations apply to α_{ij} when both i and j are greater than 1. It will be shown below that only a fraction of the condensation is due to terms containing α_{ij} (i, j > 1), so that the approximation $\alpha_{ij} \approx 1$ should be satisfactory in this case, in the absence of more exact knowledge.

Equation (1) can be written in shorter form by introducing the quantity

$$\beta_{ij} = \alpha_{ij} \, (i^{1/3} + j^{1/3})^2 \left(\frac{i+j}{ij}\right)^{1/2} , \tag{3}$$

so that

$$\text{Rate of i + j capture collision} = K T^{1/2} \beta_{ij} N_i N_j \, . \tag{4}$$

Besides the capture process, droplets may also undergo the converse vaporization or fission process. The two opposing processes, for any particular i and j, can be treated like the opposing processes in a reversible chemical reaction, so that the ratio between the two rates equals the equilibrium constant. If the mixture of molecules and droplets can be treated like a mixture of perfect gases, the equilibrium constant depends only on the temperature and can be expressed in terms of the standard free energy change*, $F^o_{i+j} - F^o_i - F^o_j$, by a well-known thermodynamic formula:[15]

---

*The term "free energy" and symbol F will be used throughout for the "Gibbs free energy," frequently also called the "thermodynamic potential." The word "potential" and symbol ∅ will be reserved for the electric circuit analogy developed in a later section.

$$\frac{\text{Rate of capture}}{\text{Rate of fission}} = \text{Equilib. const.} = \exp\left(-\frac{F^\circ_{i+j} - F^\circ_i - F^\circ_j}{kT}\right). \tag{5}$$

It follows from Eqs. (4) and (5) that

$$\text{Rate of } i + j \text{ fission} = KT^{1/2}\beta_{ij} N_{i+j} \exp\left(\frac{F^\circ_{i+j} - F^\circ_i - F^\circ_j}{kT}\right) \tag{6}$$

where F^o_{i+j} is the standard free energy of an (i + j) droplet at temperature T and at the standard concentration of one droplet per unit volume (corresponding to the units of N), and F^o_i and F^o_j are similarly defined for i and j droplets, respectively.

2.4. The General Condensation Equation

N_n, the number (per unit volume) of droplets containing n molecules, will increase with time because of capture collisions of N_i droplets with N_{n-i} droplets (i = 1, 2, .., n - 1) and because of splitting of larger droplets, N_{n+i}, into N_n and N_i (i = 1, 2, . . ., ∞), while it will be decreased by the converse processes of splitting of N_n droplets and capture of other droplets by the N_n droplets. Evaluating the rates of these four processes by use of Eqs. (4) and (6), and also remembering that N_n is the number per unit volume and hence will change if the volume V of the mixture changes, one obtains the basic differential equation for condensation:

$$\frac{dN_n}{dt} = KT^{1/2}\left\{\frac{1}{2}\sum_{i=1}^{n-1}\beta_{i,n-1}\left[N_i N_{n-i} - N_n \exp\left(\frac{F^\circ_n - F^\circ_i - F^\circ_{n-i}}{kT}\right)\right]\right.$$

$$\left. - \sum_{i=1}^{\infty}\beta_{i,n}\left[N_i N_n - N_{n+1} \exp\left(\frac{F^\circ_{n+i} - F^\circ_n - F^\circ_i}{kT}\right)\right]\right\} - \frac{N_n}{V}\frac{dV}{dt}, \tag{7}$$

where the factor 1/2 appears because the first summation counts each collision twice (since $\beta_{ij} N_i N_j = \beta_{ji} N_j N_i$, etc.). The second summation counts the n, n collisions twice, which is correct, because each such collision removes two n-molecule droplets.

Equation (7) can be simplified by introducing the quantities

$$Y_n(t) = N_n V \tag{8}$$

and

$$Q_{ij}(t) = \exp\left(\frac{F^\circ_{i+j} - F^\circ_i - F^\circ_j}{kT}\right), \tag{9}$$

so that it becomes

$$\frac{dY_n}{dt} = KT^{1/2}\left\{\frac{1}{2}\sum_{i=1}^{n-1} \beta_{i,n-i}\left(V^{-1} Y_i Y_{n-1} - Q_{i,n-i} Y_n\right) - \sum_{i=1}^{\infty} \beta_{i,n}\left(V^{-1} Y_i Y_n - Q_{i,n} Y_{n+1}\right)\right\} . \tag{10}$$

In a particular condensation situation, the vapor temperature, T, and therefore the temperature-dependent quantities Q_{ij} may be known functions of time, either because the temperature is directly controlled by some sort of cooling device, or because the cooling is produced by adiabatic expansion with a known volume change and just the earlier stages of the condensation are considered, before so much condensation has occurred that the latent heat released affects the vapor temperature. (During later stages, when the latent heat released is important, T and Q_{ij} will depend in a complicated way on the dependent variables N_n or Y_n; however, this corresponds to the macroscopic domain where, as already mentioned in section 2.1, other simplifying approximations can be made.) Thus Eq. (10) with n = 1, 2, 3, . . ., yields a set of nonlinear differential equations with variable coefficients which in principle can be solved numerically, for given initial values of Y_n, to any desired degree of accuracy. In practice, however, this procedure may be very lengthy.

2.5. The Linearized Equation and the Electrical Network Analogy

If Eq. (7) is transformed to the following variables:

$$\phi_n(t) = \left[N_1^{-n} \exp\left(\frac{F_n^\circ - nF_1^\circ}{kT}\right)\right] N_n \,; \quad \phi_1(t) = 1 \,; \tag{11}$$

$$C_n(t) = V N_1^{\,n} \exp\left(-\frac{F_n^\circ - nF_1^\circ}{kT}\right) ; \quad C_1(t) = VN_1 ; \tag{12}$$

$$R_n(t) = K^{-1} \beta_{1,n}^{-1}\, T^{-1/2}\, V^{-1} N_1^{-(n+1)} \exp\left(\frac{F_n^\circ - nF_1^\circ}{kT}\right) ; \ (n>1), \tag{13a}$$

$$R_1(t) = 2K^{-1} \beta_{1,1}^{-1}\, T^{-1/2}\, V^{-1} N_1^{-2} ; \tag{13b}$$

and the terms for i = 1 and i = n - 1 in the first summation and for i = 1 in the second summation are written out separately, the equation becomes ,

$$\begin{aligned}\frac{d(C_n\phi_n)}{dt} = {} & \frac{\phi_{n-1} - \phi_n}{R_{n-1}} - \frac{\phi_n - \phi_{n+1}}{R_n} \\ & + \frac{1}{2}\,\beta_{1,1} R_1 \left\{ \frac{1}{2} \sum_{i=2}^{n-2} \frac{\beta_{i,n-i}(\phi_i \phi_{n-i} - \phi_n)}{\beta_{1,i}\,\beta_{1,n-i}\, R_i\, R_{n-i}} \right. \\ & \left. - \sum_{i=1}^{\infty} \frac{\beta_{i,n}(\phi_i \phi_n - \phi_{n+i})}{\beta_{1,i}\,\beta_{1,n}\, R_i\, R_n} \right\}, (n>1); \end{aligned} \tag{14a}$$

$$\frac{d(C_1\phi_1)}{dt} = -\frac{\phi_1 - \phi_2}{\frac{1}{2}R_1} - \sum_{i=2}^{\infty} \frac{\phi_1\phi_i - \phi_{i+1}}{R_i} \ . \tag{14b}$$

The extra factor of two is inserted into the definition of R_1 to allow for the fact that when n = 2 there is only one term for the values i = 1 and i = n-1 in the first summation of Eq. (7). Thus a factor of 1/2 in the $(\phi_{n-1} - \phi_n)/R_{n-1}$ term in Eq. (14a) is avoided, although such a factor must then be included in other places where R_1 appears in the equations.

The terms in brackets in Eq. (14a) represent contributions due to collisions of two polymolecular aggregates, or the converse fission processes. These are usually infrequent compared to monomolecular collisions, so that to a first approximation they can be neglected, giving simply

$$\frac{d(C_n \phi_n)}{dt} = \frac{\phi_{n-1} - \phi_n}{R_{n-1}} - \frac{\phi_n - \phi_{n+1}}{R_n}, \; (n>1). \tag{15}$$

The accuracy of this approximation can be estimated a posteriori by using the ϕ's calculated from Eq. (15) to determine the size of the neglected terms. The results of such calculations will be discussed in a later section.

During the early stages of condensation, the fraction of vapor molecules which condense into liquid droplets is usually quite small, so that the total number of monomolecular vapor molecules, VN_1, remains virtually constant. Then, if the vapor volume and temperature are known functions of time, C_n and R_n defined by Eqs. (12) and (13) are known functions of time, and therefore the set of Eqs. (15), with n = 2, 3, . . ., becomes a set of first-order linear differential equations with variable coefficients.

Equations (15) are formally equivalent to the equations for the electrical network shown in Fig. 1, where the ϕ_n's are voltages,

R_n's resistances, and C_n's capacitances. This equivalence makes possible the solution of the linearized condensation equations by means of an electric analogue computer. In general, the circuit parameters R_n and C_n will vary with time, which greatly complicates the computer design; however, in certain simple cases described below, they are constant. Another difficulty in the use of an analogue computer is the necessity of measuring output voltages of the order of 10^{-10} times the input voltage. Probably this difficulty could be eliminated by introducing voltage amplifiers at intervals along the network, together with feed-back circuits so that the later stages would properly influence the earlier stages. Because of these difficulties, however, the use of an electric analogue computer has not been attempted.

One useful by-product of the electric analogy is the application of electrical concepts and terminology to the condensation problem. This makes obvious many relations which otherwise would require lengthy argument to demonstrate.

2.6. Evaluation of Droplet Free Energies

Before continuing the discussion of the condensation equation, it is helpful to determine the magnitude of the quantities R_n and C_n, which in turn depend upon the droplet free energies.

The free energy of a small liquid droplet, in excess of the free energy of the same amount of matter in the "bulk liquid," is approximately equal to the ordinary surface tension, σ, times the surface area, so that

$$F_n - nm\, F_L^\circ \approx 4\pi r^2 \sigma \approx \left(\frac{6m\sqrt{\pi}}{\rho_L}\right)^{2/3} \sigma n^{2/3}, \tag{16}$$

where F_L^o is the free energy per unit mass of a large mass of liquid under a pressure equal to its vapor pressure. The above approximation is poor when n is small and worthless when n = 1. However, an exact expression for F_1 can be found from the consideration that the free energy of the liquid equals the free energy of vapor at the saturation density, while, if the vapor is assumed to be a perfect gas, its free energy varies according to kT times the logarithm of the density.*

Hence

$$F_1 - m F_L^o = kT \log\left(\frac{N_1}{N_{sat}}\right), \tag{17}$$

where N_{sat} is the number of molecules per unit volume in a saturated vapor at the temperature T. Equations (16) and (17) can be combined to give

$$F_n - nF_1 \approx \left(\frac{6m\sqrt{\pi}}{\rho_L}\right)^{2/3} \sigma n^{2/3} - nkT \log\left(\frac{N_1}{N_{sat}}\right). \tag{18}$$

A more exact expression for the free energy of a small droplet can be obtained with the help of Tolman's theory[16] on the variation of surface tension with surface curvature. In carrying out the analysis, the utmost care must be exercised not to neglect terms of the same order of magnitude as the surface-tension correction.[17]

The total internal energy of a system consisting of a single liquid droplet surrounded by vapor in equilibrium can be regarded, following Gibbs,[18] as made up of three parts: the energy of the liquid calculated

---

*All of the logarithms used in the text are natural logarithms, to the base e = 2.718...

as if it were in a homogeneous "bulk" state and occupied the volume $4/3\,\pi r^3$, where r is the radius taken to some arbitrary point within the surface layer; the energy of the vapor calculated as if it were homogeneous and occupied the remainder of the volume; and a correction term, E_s, needed to make up the remainder of the total energy. The value of the "surface energy," E_s, depends upon the exact choice of r, which is somewhat arbitrary because of the finite thickness of the surface layer. It is desirable, however, to choose r as the radius of the well-defined "surface of tension" introduced by Gibbs, which can be considered as the surface at which the surface tension acts, so that other relations derived by Gibbs can be directly applied.

The total energy of the equilibrium liquid-vapor system can thus be written

$$E_{tot} = \frac{4}{3}\pi r^3 \rho_L E_L + \left(V - \frac{4}{3}\pi r^3\right)\rho_V E_V + E_S, \tag{19}$$

where ρ_L is the density the liquid would have in bulk at the temperature and pressure actually existing inside the droplet; E_L is the liquid energy per unit mass under the same conditions; ρ_V and E_V are the corresponding quantities for the vapor, and V is the total volume of the system. Similar expressions hold for the total entropy, S_{tot}, and the total mass, M_{tot}:

$$S_{tot} = \frac{4}{3}\pi r^3 \rho_L S_L + \left(V - \frac{4}{3}\pi r^3\right)\rho_V S_V + S_S\ , \tag{20}$$

$$M_{tot} = \frac{4}{3}\pi r^3 \rho_L + \left(V - \frac{4}{3}\pi r^3\right)\rho_V + M_S\ . \tag{21}$$

The total free energy (or thermodynamic potential) of the system is given by

$$F_{tot} = E_{tot} - TS_{tot} + p_V V = \frac{4}{3}\pi r^3 \rho_L \left(E_L + TS_L\right)$$

$$+ \left(V - \frac{4}{3}\pi r^3\right)\rho_V\left(E_V - TS_V\right) + E_S - TS_S + p_V V, \qquad (22)$$

since p_V is the pressure actually exerted on the walls of the system. For this one-component system, Gibbs' Eq. (502)[18] can be written, in the present notation,

$$E_S - TS_S = 4\pi r^2 \sigma + FM_S, \qquad (23)$$

where F is written for the common free energy (or thermodynamic potential) per unit mass of the liquid and vapor phases in equilibrium, i.e.,

$$F = E_L - TS_L + p_L/\rho_L = E_V - TS_V + p_V/\rho_V \,. \qquad (24)$$

By virtue of Eqs. (23), (24) and (21), Eq. (22) can be written

$$F_{tot} = \frac{4}{3}\pi r^3\left(\rho_L F - p_L\right) + \left(V - \frac{4}{3}\pi r^3\right)\left(\rho_L F - p_V\right)$$

$$+ 4\pi r^2 \sigma + FM_S + p_V V$$

$$= FM_{tot} + 4\pi r^2 \sigma - \frac{4}{3}\pi r^3\left(p_L - p_V\right). \qquad (25)$$

The basic surface-tension relation (Gibbs, Eq. (500)[18]) is

$$p_L - p_V = \frac{2\sigma}{r}, \qquad (26)$$

so that Eq. (25) becomes simply

$$F_{tot} = FM_{tot} + \frac{4}{3}\pi r^2 \sigma, \qquad (27)$$

The analysis of the condensation problem in earlier sections treated the vapor-droplet mixture like a mixture of perfect gases, assuming the vapor density is small. If the equivalent assumption is made here, the vapor free energy will be independent of the presence of the droplet, and hence will equal F M_V. The remainder of the total free energy given by Eq. (27) will be the free energy of the n-molecule droplet

$$F_n = nmF + \frac{4}{3}\pi r^2 \sigma, \tag{28}$$

since the mass of the droplet equals n m. In Eq. (28), F is the free energy per unit mass of the bulk liquid at a temperature T and pressure $\frac{2\sigma}{r} + p_{\text{external}}$. Since, in general,[15]

$$dF = -S\,dt + dp/\rho, \tag{29}$$

F can be evaluated in terms of the free energy, F_L^o, of the bulk liquid at temperature T and pressure equal to its ordinary vapor pressure, p_{sat} (T):

$$F = F_L^o + \int_{p_{sat}}^{\frac{2\sigma}{r} + p_{ext}} \frac{dp}{\rho_L} \quad . \tag{30}$$

If the compressibility of the liquid is neglected, this equation integrates to give

$$F = F_L^o + \frac{2\sigma}{r\rho_L} + \frac{p_{ext} - p_{sat}}{\rho_L} . \tag{31}$$

In Eq. (31), p_{ext} is the external pressure exerted on the droplet by the vapor. For saturation ratios of interest, this is not more than several times p_{sat}, so that the last term in Eq. (31) is negligible in the perfect gas approximation. With this approximation Eq. (28) can be written

$$F_n - nm F_L^{\circ} = \frac{2m\sigma n}{\rho_L r} + \frac{4}{3}\pi r^2 \sigma. \tag{32}$$

When this expression is combined with Eq. (17), one obtains finally

$$F_n - nF_1 = \frac{2m\sigma n}{\rho_L r} + \frac{4}{3}\pi r^2 \sigma - nkT\log\frac{N_1}{N_{sat}}. \tag{33}$$

The surface tension, σ, for a surface of radius r must now be evaluated. According to Tolman's theory,[16]

$$\frac{d\log\sigma}{dr} = \frac{2\sigma}{r}\left[\frac{1+\frac{\delta}{r}+\frac{1}{3}\frac{\delta^2}{r^2}}{1+2\frac{\delta}{r}+2\frac{\delta^2}{r^2}+\frac{2}{3}\frac{\delta^3}{r^3}}\right], \tag{34}$$

where δ is the distance between the Gibbs surface of tension and the surface which would make the "surface mass" vanish, i.e.,

$$\delta = \left(\frac{3nm}{4\pi\rho_L}\right)^{1/3} - r\ . \tag{35}$$

For all liquids which have been investigated,[19] δ is somewhat less than the distance between a molecule and its nearest neighbors, and thus δ/r is considerably less than 1 for droplets large enough so that the concept of surface tension is applicable. It is convenient, then, to expand Eq. (34) in powers of δ/r:

$$\frac{d\log\sigma}{dr} = \frac{2\delta}{r^2}\left[1-\frac{\delta}{r}+\frac{1}{3}\frac{\delta^2}{r^2}+\frac{2}{3}\frac{\delta^3}{r^3}-\frac{4}{3}\frac{\delta^4}{r^4}+\cdots\right]. \tag{36}$$

If this expression is integrated between r and ∞, under the assumption that δ is a constant independent of r, one obtains

$$\frac{\sigma}{\sigma_\infty} = \exp\left[-2\frac{\delta}{r} + \frac{\delta^2}{r^2} - \frac{2}{9}\frac{\delta^3}{r^3} - \frac{1}{3}\frac{\delta^4}{r^4} + \cdots\right]$$

$$= 1 - 2\frac{\delta}{r} + 3\frac{\delta^2}{r^2} - \frac{32}{9}\frac{\delta^3}{r^3} + \frac{59}{18}\frac{\delta^4}{r^4} + \cdots, \qquad (37)$$

where σ_∞ is the ordinary surface tension for a flat surface.

It is convenient to rearrange Eq. (35) to read

$$r = \left(\frac{3mn}{4\pi\rho_L}\right)^{1/3}\left(1 + \frac{\delta}{r}\right)^{-1} \qquad (38)$$

When this value for r is substituted in Eq. (32), it gives

$$F_n - nF_1 = n^{2/3}\sigma\left(\frac{6m\sqrt{\pi}}{\rho_L}\right)^{2/3}\left[\frac{1 + 2\frac{\delta}{r} + 2\frac{\delta^2}{r^2} + \frac{2}{3}\frac{\delta^3}{r^3}}{1 + 2\frac{\delta}{r} + \frac{\delta^2}{r^2}}\right]$$

$$- nkT \log\frac{N_1}{N_{sat}}\,. \qquad (39)$$

The only published attempts[20, 21, 22] to apply Tolman's theory to condensation phenomena tacitly neglect terms containing δ/r in Eq. (39), while using Eq. (34) or (37) to evaluate σ. Such a procedure is inconsistent and in general will lead to error; however, because the first order terms in δ/r fortuitously cancel in Eq. (39), the results thus obtained are first order approximations. A higher order approximation, obtained from Eqs. (37) and (39) is

$$F_n - nF_1 = n^{2/3}\sigma_\infty\left(\frac{6m\sqrt{\pi}}{\rho_L}\right)^{2/3}\left(1 - 2\frac{\delta}{r} + 4\frac{\delta^2}{r^2} - \frac{62}{9}\frac{\delta^3}{r^3} + \frac{191}{81}\frac{\delta^4}{r^4} + \cdots\right)$$

$$-nkT\log\frac{N_1}{N_{sat}}\,. \tag{40}$$

If a dimensionless quantity ϵ is defined:

$$\epsilon = \delta\left(\frac{3m}{4\pi\rho_L}\right)^{-1/3}, \tag{41}$$

which depends only upon the liquid under consideration, Eq. (35) can be transformed to give

$$\frac{\delta}{r} = \frac{\epsilon n^{-1/3}}{(1 - \epsilon n^{-1/3})} \tag{42}$$

Eq. (40) can then be written in powers of ϵ :

$$F_n - nF_1 = n^{2/3}\sigma_\infty\left(\frac{6m\sqrt{\pi}}{\rho_L}\right)^{2/3}\left(1 - 2\epsilon n^{-1/3} + 2\epsilon^2 n^{-2/3} - \frac{8}{9}\epsilon^3 n^{-1} - \frac{1}{18}\epsilon^4 n^{-4/3} + \cdots\right)$$

$$-nkT\log\frac{N_1}{N_{sat}}\,. \tag{43}$$

The function $(F_n - nF_1)$ increases from a small value when n is very small to a maximum at a point which will be called the "critical size," n_c, and then decreases and finally becomes negative for large values of n. The critical size can be found by equating the derivative of Eq. (43) to zero:

$$n_c^{1/3}\sigma_\infty\left(\frac{6m\sqrt{\pi}}{\rho_L}\right)^{2/3}\left(\frac{2}{3}-\frac{2}{3}\epsilon n_c^{-1/3}+\frac{8}{27}\epsilon^3 n_c^{-1}+\frac{1}{27}\epsilon^4 n_c^{-4/3}+\cdots\right)$$

$$-kT\log\frac{N_1}{N_{sat}}=0\ , \tag{44}$$

or, inverting the series,

$$n_c=n_{co}\left(1-3\epsilon n_{co}^{-1/3}+0\cdot\epsilon^2 n_{co}^{-2/3}+\cdots\right), \tag{45}$$

where

$$n_{co}=\frac{32\pi m^2\sigma_\infty^3}{3\rho_L^2\left(kT\log\frac{N_1}{N_{sat}}\right)^3}\ ; \tag{46}$$

n_{co} is the value n_c would have if $\epsilon = \delta = 0$. By combining Eqs. (43) and (44), one finds that

$$\left(F_n-nF_1\right)_{max(n=n_c)}=\frac{1}{3}n_c^{2/3}\sigma_\infty\left(\frac{6m\sqrt{\pi}}{\rho_L}\right)^{2/3}\left(1-4\epsilon n_c^{-1/3}+6\epsilon^2 n_c^{-2/3}\right.$$

$$\left.-\frac{32}{9}\epsilon^3 n_c^{-1}-\frac{5}{18}\epsilon^4 n_c^{-4/3}+\cdots\right). \tag{47}$$

By use of Eqs. (36) and (40), it may be shown that this result is equivalent to

$$\left(F_n-nF_1\right)_{max(n=n_c)}=\frac{4}{3}\pi r_c^2\sigma_c\ , \tag{48}$$

where r_c and σ_c are the radius and surface tension at the critical size. Since the free energy difference has a stationary value at the critical size, a droplet of this size will be in (unstable) equilibrium with the vapor. Equation (48) agrees with Gibbs' Eq. (560),[18] derived by him for the equilibrium case; one has, therefore, a check on the more general Eqs. (33) and (43), which have not, to the writer's knowledge, appeared in the literature in any form.

2.7. Incompleteness of the Macroscopically-Derived Free Energy

In the analysis of the condensation process, the vapor-droplet mixture was treated like a mixture of perfect gases. If droplets of size n behave like molecules of a perfect gas, their free energy should contain a term of the form $kT \log N_n$. It is precisely this term which permits an undersaturated or saturated vapor to contain in equilibrium a few polymolecular droplets, even though the latter have a higher "intrinsic" free energy.

Both the approximate Eq. (18) and the more exact Eq. (43) are seen to lack such a term. This deficiency is related to the fact that if either of these expressions for the free energy (setting $N_1 = 1$, for the standard state) is substituted into Eq. (11), the ratio ϕ_2/ϕ_1 will be found to depend upon the units of volume chosen, which is inconsistent with Eqs. (14) and (15) when n = 1 or 2.

A plausible way to remedy these deficiencies is to assume that, in treating the droplet thermodynamically to obtain Eq. (43), the thermal motion of the droplet as a whole was, in effect, disregarded. The additional free energy the droplet will have due to this motion can be obtained approximately from the translational and rotational partition functions[12], Z_n, for a rigid sphere of mass mn and moment of inertia of $(2/5)mn(3mn/4\pi\rho_L)^{2/3}$:

$$(Z_n)_{trans} = \frac{1}{N_n}\left(\frac{2\pi mn kT}{h^2}\right)^{3/2}, \qquad (49)$$

$$(Z_n)_{rot} = \frac{48\pi^2 (mn)^{5/2} (kT)^{3/2}}{5^{3/2} h^3 \rho_L} . \tag{50}$$

If the quantity $-kT\left[\log(Z_n)_{trans} + \log(Z_n)_{rot}\right]$ is added to Eq. (43), it becomes

$$F_n - nF_1 = n^{2/3}\sigma_\infty\left(\frac{6m\sqrt{\pi}}{\rho_L}\right)^{2/3}(1 - 2\epsilon n^{-1/3} + 2\epsilon^2 n^{-2/3}) - nkT\log\frac{N_1}{N_{sat}}$$

$$+ kT\log N_n - 4kT\log n - kT\log\left(\frac{96\sqrt{2}\,\pi^{7/2} m^4 (kT)^3}{5^{3/2} h^6 \rho_L}\right). \tag{51}$$

The terms in ϵ^3 and ϵ^4 from Eq. (43) have been omitted in Eq. (51), since they are probably smaller than the inaccuracies in the equation due to the assumption that δ is independent of r. These terms were originally calculated merely to show that their numerical coefficients are small.

The quantity which actually appears in the condensation equations is the standard free energy difference, $F_n^o - nF_1^o$, corresponding to the standard concentration of one particle per unit volume, i.e., $N_n = 1$ and $N_1 = 1$. This quantity was introduced because, in the perfect gas approximation, it depends only upon n and T, and unlike the actual free energy difference, is independent of droplet and vapor concentration. It follows from Eq. (51) that

$$\frac{F_n^o - nF_1^o}{kT} = \lambda(n^{2/3} - 2\epsilon n^{1/3} + 2\epsilon^2) + n\log N_{sat}$$

$$- 4\log n - \log\left(\frac{96\sqrt{2}\,\pi^{7/2} m^4 (kT)^3}{5^{3/2} h^6 \rho_L}\right), \tag{52}$$

where, for convenience, λ designates the dimensionless surface-tension factor:

$$\lambda(T) = \frac{\sigma_\infty}{kT}\left(\frac{6m\sqrt{\pi}}{\rho_L}\right)^{2/3} . \tag{53}$$

If this expression is substituted into Eq. (11), the resulting ϕ_n are independent of the dimensional units used.

An alternative method of introducing the $kT \log N_n$ term, which appears nearly as plausible, is to assume that Eq. (43) gives the free energy for a droplet confined to a volume of order mn/ρ_L. If this volume is then expanded to $1/N_n$, and the droplet behaves like a perfect gas molecule, the resulting isothermal change in the free energy is $kT \log N_n + kT \log (mn/\rho_L)$. If this expression is added to Eq. (43), the standard free energy difference becomes

$$\frac{F_n^\circ - nF_1^\circ}{kT} = \lambda\left(n^{2/3} - 2\epsilon n^{1/3} + 2\epsilon^2\right) + n \log N_{sat} + \log n - \log\left(\frac{\rho_L}{m}\right) , \tag{54}$$

instead of Eq. (52).

Equations (52) and (54) are certainly not equivalent, although, surprisingly enough, the two expressions are approximately equal for many cases of physical interest. A third, still different expression for the standard free energy difference will be obtained in section 2.8. Equivalent discrepancies appear in the condensation relations derived by previous investigators, depending upon their different approaches.*

---

*Compare, for example, Frenkel,[12] p. 384, Eq. (16a) with his unnumbered equation for N_g on p. 381.

These differences arise basically from the attempt to extrapolate macroscopic relations to the molecular domain. In the determination of droplet free energies as a function of n, macroscopic measurements enable evaluation of the "bulk" term proportional to n, the surface-tension term proportional to $n^{2/3}$, and probably, from Tolman's theory, the next order correction term, proportional to $n^{1/3}$. Terms of lower order, however, such as constant terms or terms proportional to log n, may be completely masked and not measurable by any direct macroscopic means. Such lower order terms can make a considerable difference in condensation processes.

At least two approaches toward evaluating such terms are possible. On the one hand, the condensation theory might be worked out for various assumed values of the free energy, and the results compared with experiment. This procedure is followed in the present paper. On the other hand, the free energy of very small droplets might be calculated directly from the principles of statistical mechanics and quantum mechanics. Carrying out the latter procedure is a formidable task; a beginning has recently been made by Reed,[23] who calculated the free energy for nitrogen aggregates containing 2, 3, 4, 5, 6 and 8 molecules, assuming a Lennard-Jones interaction potential between two molecules and making other approximations. In Figs. 2 and 3, Reed's values of $(F_n^o - nF_1^o)/kT$ are compared with values calculated from Eqs. (52) and (54), and also with values from an alternate equation derived in section 2.8. The comparison will be discussed in detail later. In any case, these free energy values for a single substance over a limited range of n are hardly sufficient to determine which of the alternate expressions is most accurate in general. All of the expressions, however, are of the following form:

$$\frac{F_n^\circ - nF_1^\circ}{kT} = \lambda\left(n^{2/3} - 2\epsilon n^{1/3}\right) + n \log N_{sat}$$

$$+ A \log n - \log B, \quad (n>1) \tag{55}$$

where A and B are quantities independent of n. A is a positive or negative quantity of order unity; B is a large positive quantity of order 10^{20} cm^{-3}. When accurate values of the free energy for n = 2, 3, ... are known, terms proportional to $n^{-1/3}$, $n^{-2/3}$, etc., might be added to Eq. (55) to obtain better agreement; however, it is probably easier to work directly with the numerical free energies for the first few values of n, and use Eq. (56) for larger values of n.

The theoretical condensation relations developed in this paper will be derived first in terms of arbitrary free-energy functions, and then specialized to the functional form of Eq. (55). Specific values of A and B will be assumed only for the numerical calculations. Thus, the theory remains readily adaptable to any more accurate free-energy values which future investigators may obtain.

2.8. The Condensation Equations in Terms of Droplet Vapor Pressures

Becker and Döring[5] developed their theory of condensation in terms of the vapor pressures of small droplets instead of their free energies, and used the Gibbs-Thomson formula for the variation of vapor pressure with droplet radius. Basically, the two approaches are equivalent, if both are carried out without approximation. It is natural, however, to make different types of approximations in the two cases, so that the usual results are only approximately equivalent. If only a rough answer is required, the Becker-Döring approach is in some ways simpler and follows physical intuition more closely. If a better approximation is desired, however, the development of the theory in terms of free-energy differences has two important advantages. In the first place, the nonlinear terms in the condensation equation, representing consolidation or fission of polymolecular droplets, can be written down immediately in terms of the free energies, but could be obtained only by a very involved argument in terms of the droplet vapor pressures. Secondly, the free energy of an n-molecule aggregate or droplet is a definite well-defined quantity (even though its numerical value may not be known precisely). The vapor pressure of an n-molecule droplet, on the other hand, might be defined in several different ways; for example, in terms of equilibrium between n and (n - 1) molecule droplets, or between n and (n + 1) molecule droplets, and with or without a factor $[n/(n \pm 1)]^{2/3}$ to allow for the difference in surface areas, etc. For small n, these definitions are not equivalent, and the calculated rates of condensation will depend somewhat upon which vapor pressure is assumed to be given by the extrapolated Gibbs-Thomson formula. Significant errors may also result from the mixed use of two different definitions of vapor pressure.

The vapor-pressure definition appropriate to the Becker-Döring theory can be readily derived. Becker and Doring expressed the rate of growth of (n - 1) molecule droplets to n-molecule droplets as $Kk^{-1}T^{-1/2}(n-1)^{2/3}pN_{n-1}$ (in the present notation), where p is the pressure of the monomolecular vapor. Since $p = N_1kT$, this expression is seen to agree with Eq. (4) when $i = 1$, $j = n - 1$, and $\beta_{1,n-1} = (n-1)^{2/3}$. For the rate of the converse process, the decay of n-molecule droplets to (n - 1), they used $Kk^{-1}T^{-1/2}n^{2/3}P_nN_n$, where P_n is the "vapor pressure" of an n-molecule droplet. By comparison with Eq. (6), setting i = 1, j = n - 1, and $\beta_{1,n-1} = (n-1)^{2/3}$ again, it is seen that

$$P_n = kT\left(\frac{n-1}{n}\right)^{2/3} \exp\left(\frac{F_n^\circ - F_{n-1}^\circ - F_1^\circ}{kT}\right). \tag{56}$$

If P_∞ denotes the ordinary vapor pressure over a flat surface,

$$P_\infty = N_{sat}\, kT, \tag{57}$$

so that

$$\frac{P_n}{P_\infty} = \frac{1}{N_{sat}}\left(\frac{n-1}{n}\right)^{2/3} \exp\left(\frac{F_n^\circ - F_{n-1}^\circ - F_1^\circ}{kT}\right) \tag{58a}$$

$$= \left(\frac{n-1}{n}\right)^{2/3} \exp\left(\frac{F_n^\circ - F_{n-1}^\circ - F_{sat}}{kT}\right). \tag{58b}$$

Equation (58b) differs by the factor $[(n-1)/n]^{2/3}$ from the definition of P_n/P_∞ used by Reed.[23]

By taking the products of Eq. (58a) for consecutive values of n, one finds, on simplification

$$\prod_{i=2}^{n}\left(\frac{P_i}{P_\infty}\right) = N_{sat}^{-(n-1)}\, n^{-2/3} \exp\left(\frac{F_n^\circ - nF_1^\circ}{kT}\right), \tag{59}$$

$$\frac{F_n^\circ - nF_1^\circ}{kT} = (n-1)\log N_{sat} + \frac{2}{3}\log n + \sum_{i=2}^{n}\log\left(\frac{P_i}{P_\infty}\right). \tag{60}$$

Becker and Döring further assumed that, even for small values of n, P_n/P_∞ can be approximated by the Gibbs-Thomson formula:[15]

$$\log\left(\frac{P_n}{P_\infty}\right) = \frac{2\sigma m}{\rho_L kTr}. \tag{61}$$

Equation (61) was first deduced by W. Thomson from mechanical considerations, and later derived more rigorously by Gibbs,[18] using a free-energy argument. When values of r from Eq. (38), σ from Eq. (37), δ/r from Eq. (42) and λ from Eq. (53) are substituted into Eq. (61), one obtains

$$\log\left(\frac{P_n}{P_\infty}\right) = \lambda\left(\frac{2}{3}n^{-1/3} - \frac{2}{3}\epsilon n^{-2/3} + 0\cdot\epsilon n^{-1}\right), \tag{62}$$

neglecting higher order terms. Substitution of values for $\log(P_i/P_\infty)$ from Eq. (62) into Eq. (60) yields

$$\frac{F_n^\circ - nF_1^\circ}{kT} = \lambda\sum_{i=2}^{n}\left(\frac{2}{3}i^{-1/3} - \frac{2}{3}\epsilon i^{-2/3}\right) + (n-1)\log N_{sat} + \frac{2}{3}\log n. \tag{63}$$

The summations in Eq. (64) can be expressed with the help of a series for the Riemann Zeta-function (Jahnke and Emde,[24] p. 269):

$$1+\sum_{i=2}^{n} i^{-z} = \frac{1}{1-z}n^{1-z} + \zeta(z) + \frac{1}{2}n^{-z} + \cdots, \quad (z \neq 1). \tag{64}$$

Thus, Eq. (63) becomes, to the same order of approximation,

$$\frac{F_n^\circ - nF_1^\circ}{kT} = \lambda\left(n^{2/3} - 2\epsilon n^{1/3} - 1.313 + 2.291\epsilon\right)$$

$$+ (n-1)\log N_{sat} + \frac{2}{3}\log n. \qquad (65)$$

Eq. (65) is seen to be of the form of Eq. (55), with

$$A = \frac{2}{3} \qquad (66)$$

and

$$B = N_{sat}\ \exp\left[\lambda\,(1.313 - 2.291\epsilon)\right]. \qquad (67)$$

In their treatment, Becker and Döring simply approximated the summation in Eq. (63) (without the ϵ terms) by the corresponding integral between the limits 1 and n, and obtained results equivalent to $\epsilon = 0$, $A = 2/3$, $B = N_{sat}\exp(\lambda)$.

2.9 . The Equilibrium Solution of the Condensation Equations

We return now to consideration of the condensation process and its electrical analogue. If the resistances and capacitances of the electrical network shown in Fig. 1 do not vary with time, a possible solution for the network is obtained simply by giving all the voltages the same constant value. Since $\phi_1 = 1$ from Eq. (11), the above condition becomes

$$\phi_n = 1 \quad \text{(for all n)}. \qquad (68)$$

This solution evidently corresponds to the case when there is no current flow in the electrical analogy, or no net growth of droplets in the condensation situation, i.e., an equilibrium state has been attained. Holding the resistances and capacitances fixed corresponds to holding the temperature and volume of the vapor fixed, according to Eqs. (12) and (13).

Equation (68) is readily seen to be a solution not only of the linearized Eq. (15), but also of the exact nonlinearized Eqs. (14a) and (14b). This result is to be expected, because it is equivalent to the well-known chemical principle that the equilibrium of an over-all reaction is independent of the assumed intermediate stages.

The number of droplets of a given size in the equilibrium situation is found from Eqs. (11) and (68) to be

$$N_n = N_1{}^n \exp\left(-\frac{F_n^\circ - n F_1^\circ}{kT}\right). \tag{69}$$

If free energy values from Eq. (55) are substituted into Eq. (69), one obtains

$$N_n = B n^{-A} s^n \exp\left[-\lambda\left(n^{2/3} - 2\epsilon n^{1/3}\right)\right], \tag{70}$$

where s is the saturation ratio:

$$s = \frac{N_1}{N_{sat}} \quad . \tag{71}$$

When $s \neq 1$, Eq. (70) shows that the series $\sum_{n=1}^{\infty} N_n$, which expresses the total number of droplets of all sizes per unit volume, behaves like the geometric series $\sum_{n=1}^{\infty} s^n$, converging for undersaturated vapors ($s < 1$) and diverging for supersaturated vapors ($s > 1$). For saturated vapors ($s = 1$), the series behaves like $\sum_{n=1}^{\infty} \exp(-n^{2/3})$ and hence converges. It follows that the equilibrium state is physically realizable for undersaturated and saturated vapors, but not for supersaturated vapors. In the realizable cases the values of N_n fall off rapidly with increasing n, and generally become negligible for $n > 10$.

Equations (69) and (70) for the equilibrium droplet distribution do not contain the β_{ij}'s, and hence are independent of the uncertainties in numerical value of these quantities. They do, however, contain the free energy difference as an exponent, and thus the calculated values of equilibrium N_n can differ by factors of 10 to 1000 depending upon which free energy expression is used, i.e., upon the values of A and B assumed in Eq. (70).

2.10. The Steady-State Solution

If R_n and C_n are held constant, a time-independent solution of the linearized Eq. (15) may be sought by equating the left hand side to zero. This procedure yields

$$\frac{\phi_{n-1} - \phi_n}{R_{n-1}} = \frac{\phi_n - \phi_{n+1}}{R_n}, \qquad \text{(for all n)} \tag{72}$$

or in other words,

$$\frac{\phi_n - \phi_{n+1}}{R_n} = constant = JV. \tag{73}$$

The constant in Eq. (73) is denoted by J V because it can be shown that J is then the steady rate at which droplets grow from any size n to n + 1. This result follows from the fact that $C_n \phi_n = V N_n$, according to Eqs. (11) and (12); thus the left hand side of Eq. (15) equals $V\,dN_n/dt$ (since V is constant in the steady state), and the terms on the right hand side must then represent "droplet-growth currents" multiplied by V. If Eq. (73) is written in the form

$$\phi_i - \phi_{i+1} = JVR_i \tag{74}$$

and the result is summed from $i = 1$ to $i = n - 1$, all ϕ's except the first and last will cancel, yielding

$$\phi_1 - \phi_n = JV\sum_{i=1}^{n-1} R_i \quad . \tag{75}$$

Solving for J, and using $\phi_1 = 1$, one obtains

$$J = \frac{1-\phi_n}{V\sum_{i=1}^{n-1} R_i} \quad . \tag{76}$$

Equation (76) holds for any value of n. By Eq. (11), $\phi_n =$ $= N_n N_1^{-n} \exp\left[(F_n^o - nF_1^o)/kT\right]$. As n becomes large, Eq. (55) shows that this expression behaves like $N_n s^{-n}$. If N_n is bounded, which must be true in any physical situation, then $\lim_{n\to\infty} \phi_n = 0$ for supersaturated vapors ($s > 1$). Thus, by letting $n \to \infty$, Eq. (76) becomes, for supersaturated vapors,

$$J = \frac{1}{V\sum_{n=1}^{\infty} R_n} \tag{77}$$

The summation in the denominator of Eq. (77) behaves like $\sum_{n=1}^{\infty} s^{-n}$, and hence converges. For an undersaturated or saturated vapor, both numerator and denominator of Eq. (76) become large for large n, but their ratio is of order N_n. If $\lim_{n\to\infty} N_n = 0$, since, physically, a droplet of infinite size cannot be found in any finite volume, then it can be shown that J = 0 for undersaturated or saturated vapors, as anticipated.

Equation (77) can also be obtained readily from the electric circuit analogy. If the circuit of Fig. 1 is in a steady state, the charges on the capacitances remain constant, so that the capacitances can be omitted without changing the physical situation, leaving just a voltage $\phi_1 - \phi_\infty = 1$ across the series resistances R_n. The electric current flowing is evidently $1/\sum_{n=1}^{\infty} R_n$, assuming that the summation converges. The electric current differs from the "droplet current" by the factor V, so that Eq. (77) is again obtained. (It might be noted that for the steady state, since V = constant, one can set V = 1 without loss of generality.) This simplified electrical analogy was discovered by Becker and Döring.[5]

The value of $V\sum_{n=1}^{\infty} R_n$ needed to calculate J can be found with the help of Eq. (55):

$$V\sum_{n=1}^{\infty} R_n = \frac{1}{KBT^{1/2}N_1}\left\{\frac{2B}{\beta_{1,1}N_1} + \sum_{n=2}^{\infty} \frac{n^A s^{-n}}{\beta_{1,n}} \exp\left[\lambda\left(n^{2/3} - 2\epsilon n^{1/3}\right)\right]\right\}. \quad (78)$$

For large values of n, $\alpha_{1,n} = 1$ (see section 2.3), and therefore $\beta_{1,n} \approx n^{2/3}$ by Eq. (3). Equation (78) would be simplified if $\beta_{1,n} = n^{2/3}$ even for small values of n; this corresponds to $\alpha_{1,n} = (1 + n^{-1/3})^{-2}\,(1 + n^{-1})^{-1/2}$. A curve for this expression is shown in Fig. 4; it increases from 0.25 at n = 2 to approach 1 asymptotically as n approaches infinity. This is not an unreasonable assumption for $\alpha_{1,n}$, when more accurate information is lacking. If, on the other hand, it is believed that actually $\alpha_{1,n} = 1$, the approximation $\beta_{1,n} = n^{2/3}$ is equivalent to neglecting the radius of the vapor molecules compared to the droplet radius, and neglecting the thermal motion of the droplets.

With this approximation, Eq. (78) can be written

$$V\sum_{n=1}^{\infty} R_n = \frac{1}{KT^{1/2}N_1 B}\left\{\frac{2B}{\beta_{1,1}N_1} + \sum_{n=2}^{\infty} \exp\left[-n\log\Delta + \lambda\left(n^{2/3} - 2\epsilon n^{1/3}\right) + \left(A - \frac{2}{3}\right)\log n\right]\right\} . \tag{79}$$

The terms in this summation have a maximum for a certain value of n which will be designated by n_*, and which can be found by equating the derivative with respect to n of the exponent in Eq. (79) to zero:

$$-\log\Delta + \frac{2}{3}\lambda\left(n_*^{-1/3} - \epsilon n_*^{-2/3}\right) + \left(A - \frac{2}{3}\right)\frac{1}{n_*} = 0 , \tag{80}$$

$$n_* = n_{*0}\left[1 - 3\epsilon n_{*0}^{-1/3} + \frac{9}{2\lambda}\left(A - \frac{2}{3}\right)n_{*0}^{-2/3} + \cdots\right] , \tag{81}$$

where

$$n_{*0} = \left(\frac{2\lambda}{3\log\Delta}\right)^3 = n_{c0} . \tag{82}$$

The quantity n_* differs from the "critical size," n_c defined previously, in that n_* is defined to maximize a quantity which has an additional term $(A - \frac{2}{3})$ log n compared to the corresponding quantity for n_c. In the Becker-Döring approximation, $A = 2/3$ and thus $n_* = n_c$, which result can also be obtained by comparing Eqs. (45) and (81).

Because of their exponential character, the terms in Eq. (78) or (79) decrease rapidly on either side of n_*, so that only the terms near the maximum need to be considered to obtain a reasonably accurate value of J. Moreover, when n_* is not extremely small, the initial term $2B/(\beta_{1,1}N_1)$ and the next few terms are negligible compared to later terms, so that the calculated value of J is practically independent of the uncertainties in the magnitude of the first few accommodation coefficients, $\alpha_{1,1}$, $\alpha_{1,2}$, etc. Thus, whether these coefficients for $n \leq 5$ are closer to unity or to 10^{-3} ordinarily makes little difference; however, if they should be as small as 10^{-6} the reduction in J would be appreciable for high saturation ratios when n_* is of the order of 10 or 20.

If a simpler expression for J is desired, the summation in Eq. (79) may be approximated by the corresponding integral, with an error which is small when n_* is reasonably large. Denote by f(n) the terms in the summation, i.e.,

$$f(n) = \exp\left[-n \log s + \lambda\left(n^{2/3} - 2\epsilon n^{1/3}\right) + \left(A - \tfrac{2}{3}\right)\log n\right]. \tag{83}$$

It is convenient to introduce a new variable, x, by the equation

$$n = n_* (1+x)^3, \tag{84}$$

so that x = 0 when $n = n_*$ and f(n) = maximum. In terms of this variable,

$$f(n) = f(n_*) \exp\left[-n_*\left(3x + 3x^2 + x^3\right)\log s + \lambda n_*^{2/3}\left(2x + x^2\right) - 2\epsilon n_*^{1/3} x + (3A-2)\log(1+x)\right]. \tag{85}$$

If Eq. (80) is multiplied by $3n_* x$ and subtracted from the exponent of Eq. (85), the latter reduces to

$$f(n) = f(n_*) \exp\left\{- Kx^2 - n_* x^3 \log s + (3A-2)\left[\log(1+x) - x\right]\right\}, \tag{86}$$

where

$$K = 3n_* \log s - \lambda n_*^{2/3} = \frac{3}{2} n_{*0}\left[1 - 4\epsilon n_{*0}^{-1/3} + (\epsilon^2 + 6A - 4) n_{*0}^{-2/3}\right], \qquad (87)$$

by virtue of Eqs. (81) and (82). Hence

$$\int_2^\infty f(n)\,dn = 3n_* f(n_*) \int_{-1+\left(\frac{2}{n_*}\right)^{1/3}}^{\infty} \exp\left[-Kx^2 - n_* x^3 \log s + 3A \log(1+x) - (3A-2)x\right] dx\,. \qquad (88)$$

The integrand on the right-hand side of Eq. (88) has a value of unity at x = 0, while it has a value less than 0.01 when $|x| > 1/2$, assuming the usual situation that $n_* \log s > 10$. Thus, with an error usually less than 1%, Eq. (88) can be written

$$\int_2^\infty f(n)dn = 3n_* f(n_*) \int_{-1/2}^{+1/2} \exp\left[-Kx^2 - n_* x^3 \log s + 2x - \frac{3}{2}Ax^2 + Ax^3 - \cdots\right] dx$$

$$= 3n_* f(n_*) \int_{-1/2}^{+1/2} \left[1 + 2x + \left(A - \frac{8}{3} - n_* \log s\right)x^3 + \cdots\right] \exp\left[-\left(K + \frac{3}{2}A - 2\right)x^2\right] dx. \qquad (89)$$

The exponent in Eq. (89) was chosen so as to make the x^2 term in the brackets vanish. The contributions to the integral from the x, x^3, x^5, ... terms are zero by symmetry. If the x^4, x^6, ... terms are neglected, only the exponential remains under the integral sign. The limits of integration can now be extended to ± ∞ with negligible error, so that

$$\int_2^{\infty} f(n)\,dn = 3n_* f(n_*) \int_{-\infty}^{\infty} \exp\left[-\left(K + \tfrac{3}{2}A - 2\right)x^2\right] dx$$

$$= 3\pi^{1/2} n_* f(n_*) \left(K + \tfrac{3}{2}A - 2\right)^{-1/2} . \tag{90}$$

The expression for J then becomes, if the $2B/(\beta_{1,1}N_1)$ term in Eq. (79) is neglected,

$$J = \left(\frac{KBT^{1/2}N_{sat}}{3\pi^{1/2}}\right) \frac{s\left[3n_* \log s - \lambda n_*^{2/3} + \tfrac{3}{2}A - 2\right]^{1/2}}{(n_*)^{A+1/3}}$$

$$\times \exp\left[n_* \log s - \lambda\left(n_*^{2/3} - 2\epsilon n_*^{1/3}\right)\right] . \tag{91}$$

Equation (91) corresponds to the simplifying assumption that $\beta_{1,n} = n^{2/3}$ in the region $n \sim n_*$. If the different assumption that $\alpha_{1,n} = 1$ is made, so that

$$\beta_{1,n} = n^{2/3}\left(1 + n^{-1/3}\right)^2 \left(1 + n^{-1}\right)^{1/2} , \tag{92}$$

then the value obtained for J will be slightly larger. Such an assumption corresponds to multiplying the integrand of Eq. (89) by a factor $(1 + n^{-1/3})^{-2}(1 + n^{-1})^{-1/2} = (1 + n_*^{-1/3})^{-2} + 2n_*^{-1/3}x - 2n_*^{-1/3}x^2 + \ldots$ The resulting value of J is, to a good approximation,

$$J = \left(\frac{KT^{1/2}BN_{sat}}{3\pi^{1/2}}\right) \frac{s\left[3n_* \log s - \lambda n_*^{2/3} + \tfrac{3}{2}A - 2 - 2n_*^{-1/3}\right]^{1/2}}{(n_*)^{A+1/3}}$$

$$\times \left(1 + n_*^{-1/3}\right)^2 \exp\left[n_* \log s - \lambda\left(n_*^{2/3} - 2\epsilon n_*^{1/3}\right)\right] , \tag{93}$$

instead of the value given by Eq. (91).

It is of interest to compare Eqs. (91) and (93) with the result obtained by Becker and Döring.[5] They obtained, in the present notation

$$J = \left(\frac{K T^{1/2} N_{sat}^{2}}{3\pi^{1/2}}\right) s^{2} \lambda^{1/2} n_{*o}^{-1/3} \exp\left(-\tfrac{1}{3} \lambda n_{*o}\right). \qquad (94)$$

Because they were interested only in a very rough answer, Becker and Döring dropped a factor equal to e^{λ}/s, which generally has a magnitude of 10 to 1000, in situations of physical interest. Aside from this factor, Eq. (94) is a good approximation to Eq. (91) when $A = 2/3$, $B = N_{sat} e^{\lambda}$, $\epsilon = 0$ and $n_{*} = n_{*o}$. Equation (94) differs from Eq. (92) by an additional factor, $(1 + n_{*}^{-1/3})^{-2}$, because Becker and Döring neglected the finite radius of the vapor molecules in computing capture collisions.

The number of droplets of a given size, in the steady-state situation, is easily derived from Eqs. (76), (11) and (13):

$$\phi_n = 1 - JV \sum_{i=1}^{n-1} R_i , \qquad (95a)$$

$$\phi_n = JV \sum_{i=n}^{\infty} R_i ; \qquad (95b)$$

$$N_n = N_1^{\,n} \exp\left(-\frac{F_n^{\circ} - n F_1^{\circ}}{kT}\right) JV \sum_{i=n}^{\infty} R_i , \qquad (96a)$$

$$N_n = \frac{KT^{1/2} V N_1 \beta_{1,n} \sum_{i=n}^{\infty} R_i}{R_n \sum_{i=1}^{\infty} R_i} . \qquad (96b)$$

The different forms of these equations are useful for different purposes.

The steady-state solution has been derived above for the linearized Eq. (15). The effect of the nonlinear terms in the more exact Eq. (14a) will be to increase J slightly, since both linear and nonlinear terms tend to make the ϕ_n approach the equilibrium value $\phi_n = 1$ (see section 2.9), and this results in a "current flow" toward larger values of n. On the basis of a numerical calculation, discussed later, the contribution of the nonlinear terms to J is estimated to be only a few per cent in most practical cases.

Thus far, the steady state has been discussed as a possible mathematical solution to the condensation equations, without inquiring as to whether such a state is physically realizable. If a supersaturated vapor were maintained at constant volume and temperature, and all droplets which grew very large were removed and replaced by an equal mass of vapor molecules, it is evident that the system, in time, would approach such a steady state. In the electrical analogy, this corresponds to supplying a constant potential at ϕ_1 and grounding a particular ϕ_n (n large). Because the R_n decrease rapidly beyond the critical n, the result is practically independent of the choice of the voltage ϕ_n which is grounded (or of the droplet size which is removed) provided that n is at least twice the critical size, n_*.

Such a physical situation, involving constant removal of droplets and addition of vapor, seldom, if ever, occurs in practice. Previous investigators,[1-9] however, have used the steady-state value of J to determine the occurrence or nonoccurrence of condensation in many types of unsteady physical situations. Because of the exponential factor in Eqs. (91) and (92), a small variation in temperature or saturation ratio generally causes a large variation in J, so that in many practical situations very rough approximations in J are permissible. It is not obvious, however, that typical unsteady condensation situations can be even roughly approximated by a steady state, and the arguments of previous investigators on this point have been vague and rather unconvincing. This question will be discussed in the next section.

2.11. Time-Dependent Solutions of the Condensation Equations

In a general condensation situation, the volume V should be a known function of time, and the temperature T either known directly (as when the system is in a thermal bath) or determined by adiabatic expansion laws, radiation laws, etc., or determined by these laws plus terms due to latent heat released, if this effect is significant. In the first two cases, the condensation Eq. (15) is linear with variable coefficients; in the last case it is nonlinear. In all of these cases, the electric circuit analogue involves resistances and capacitances which vary with time. In general, the only recourse appears to be to solve the differential equations numerically, and for this purpose Eq. (10) is probably better suited than Eq. (15).

There exists, however, a particular nonsteady condensation situation which is considerably simpler to treat than the most general case. This is the situation when an undersaturated or saturated vapor is suddenly brought to a supersaturated state (by adiabatic expansion or otherwise), so rapidly that negligible growth of droplets occurs during the transition period, and thereafter the volume and temperature of the vapor are held constant while the droplet-growth process occurs. The quantities C_n and R_n then remain constant during the period of significant condensation, and the nonsteady character of the process is reflected only in the specification of nonequilibrium initial values of the dependent parameters, $\phi_n(t)$.

The assumption will be made that, before the vapor is cooled to supersaturation, it is first held in a particular undersaturated or saturated state long enough for the corresponding equilibrium distribution of droplets to be obtained. (Since N_n is generally negligible under these conditions when $n > 10$, the time required is only that necessary to establish equilibrium among the droplets having $n \leq 10$, which is usually less than 10^{-7} sec.) The number of droplets in this equilibrium state is given by Eq. (69) or (70). If, at $t = 0$, the volume and temperature of the vapor are changed so suddenly that the total number of droplets, VN_n, of each size, is conserved, the new number of droplets per unit volume will be given by

$$N_n(0) = \left(\frac{\bar{V}}{V}\right) \bar{N}_1^{-n} \exp\left(-\frac{\bar{F}_n^\circ - n\bar{F}_1^\circ}{kT}\right) \tag{97a}$$

$$= \frac{\bar{V}}{V} \bar{B} n^{-A} (\bar{s})^n \exp\left[-\bar{\lambda}\left(n^{2/3} - 2\bar{\epsilon} n^{1/3}\right)\right], \quad (n > 1), \tag{97b}$$

where a bar is used to distinguish the parameters of the old undersaturated or saturated state ($\overline{V}$, $\overline{N}_1$, $\overline{T}$, etc.) from the corresponding parameters of the new supersaturated state (V, N_1, T, etc.). The initial values of ϕ_n can then be obtained with the help of Eqs. (11) and (55):

$$\phi_n(0) = \left(\frac{V}{\overline{V}}\right)^{n-1} \exp\left(\frac{F_n^\circ - nF_1^\circ}{kT} - \frac{\overline{F}_n^\circ - n\overline{F}_1^\circ}{k\overline{T}}\right) \tag{98a}$$

$$= \left(\frac{\overline{V}\overline{B}}{VB}\right)\left(\frac{\bar{s}}{s}\right)^n \exp\left[(\lambda - \bar{\lambda})n^{2/3} - 2(\lambda\epsilon - \bar{\lambda}\bar{\epsilon})n^{1/3}\right], (n > 1) \tag{98b}$$

Like $N_n(0)$, the values of $\phi_n(0)$ decrease rapidly with increasing n, and generally become negligible for $n > 10$. For the significant cases when $n \leq 10$, Eq. (98b) may be only a rough approximation to the exact Eq. (98a); however, it will be shown below that a considerable error in the initial values, $\phi_n(0)$, usually produces only a small change in the calculated condensation process.

During the subsequent condensation process, since V and T are held constant, the parameters C_n and R_n remain constant as long as the total amount of condensation is so small that there is negligible depletion of the vapor molecules, i.e., negligible decrease in N_1. Eventually, in a physical condensation situation, the vapor depletion will become significant, and also the latent heat released on condensation will become large enough to affect the temperature; however, it will be shown that by this time virtually all of the droplets have grown to a size sufficiently large so that their further growth can be calculated by means of simple macroscopic diffusion and heat-conduction relations.

In treating the condensation, it is convenient to introduce a dimensionless time parameter:

$$\tau = K T^{1/2} N_1 t , \tag{99}$$

and rewrite Eq. (15) to read

$$\frac{d\phi_n}{d\tau} = a_n \phi_{n+1} - (a_n + b_n)\phi_n + b_n \phi_{n-1} , (n>1), \tag{100}$$

where the C_n and R_n have been combined into the quantities

$$a_n = \left[K T^{1/2} N_1 C_n R_n\right]^{-1} = \beta_{1,n} \quad , (n>1), \tag{101}$$

$$\begin{aligned} b_n &= \left[K T^{1/2} N_1 C_n R_{n-1}\right]^{-1} = \beta_{1,n-1} N_1^{-1} \exp\left(\frac{F_n^\circ - F_{n-1}^\circ - F_1^\circ}{kT}\right) \\ &= \beta_{1,n-1} \mathcal{S}^{-1} \left(\frac{n}{n-1}\right)^A \exp\left[\lambda n^{2/3} - \lambda (n-1)^{2/3} - 2\epsilon\lambda n^{1/3} + 2\epsilon\lambda (n-1)^{1/3}\right], (n>2), \end{aligned} \tag{102a}$$

$$\begin{aligned} b_2 &= \frac{1}{2} \beta_{1,1} N_1^{-1} \exp\left(\frac{F_2^\circ - 2F_1^\circ}{kT}\right) \\ &= (2)^{A-1} \beta_{1,1} \mathcal{S}^{-1} \left(\frac{N_{sat}}{B}\right) \exp\left(2^{2/3}\lambda - 2^{4/3}\epsilon\lambda\right). \end{aligned} \tag{102b}$$

In the Becker-Döring type of approximation, $\beta_{1,n} = n^{2/3}$ and the free energies are given by Eq. (63), so that the above expressions simplify to

$$a_n = n^{2/3} \quad , (n>1), \tag{103}$$

$$b_n = n^{2/3} \mathcal{S}^{-1} \exp\left[\frac{2}{3} \lambda \left(n^{-1/3} - \epsilon n^{-2/3}\right)\right], (n>2), \tag{104a}$$

$$b_2 = 2^{-1/3} s^{-1} \exp\left[\frac{2}{3} \lambda \left(2^{-1/3} - 2^{-2/3} \epsilon\right)\right]. \tag{104b}$$

Because of the rather complicated variation of b_n with n (even in the simplest case when $\epsilon = 0$), it has not been possible to find a general analytic solution for the infinite set of Eqs. (100), with $n = 2, 3, 4, \ldots$, or even a particular solution which satisfies the necessary condition $\phi_1 = 1$. One must therefore turn to analytic approximations or numerical methods. A possible approximation is the neglect of all ϕ's beyond a certain ϕ_n. If the n in ϕ_n is chosen to be considerably larger than ten, one may expect that there will be a certain period of time during which this approximation is valid, since only a negligible number of droplets containing more than ten molecules is present initially. The length of this period may be estimated by noting the time during which ϕ_n, the last term not dropped, is negligible. If n is chosen to be more than twice the critical size, ϕ_n will always be negligible compared to the ϕ's near critical size so that the entire behavior of droplets near the critical size can be obtained. The continuing rate of growth of droplets beyond the critical size, however, can be obtained only by increasing n so that it always exceeds the droplet size of interest.

With this approximation, Eqs. (100) become a finite set of first-order linear differential equations with constant coefficients, which can be solved by standard methods.* The steady-state solution is first subtracted off to remove the nonhomogeneous condition on ϕ_1; the remainder of the solution is then of the form $\sum_{i=2}^{n} c_i e^{-\mu_i \tau}$, where the c_i's are determined by the initial conditions and the μ_i's are the roots of a

---

*See, for instance, Carslaw and Jaeger,[25] pp. 83-86.

secular equation of order n - 1. In typical cases of physical interest, when n must be of the order of 100 to cover the critical region, this procedure involves a vast amount of computation. It has been found possible to derive a recurrence relation for the secular determinants of successive orders which considerably simplifies the determination of the μ_i's. When the μ_i's were computed for a typical case having n = 50, with the help of a punched-card computing machine, an even more serious diffifulty arose. It was found that the summations expressing the desired ϕ's contained many large terms which nearly cancelled to give totals several orders of magnitude smaller. In some cases, eight to ten significant figures had to be carried in intermediate calculations to obtain results correct to 50%. Further investigation showed that this difficulty arises because of the large variation in magnitude of R_n with n which is inherent in the condensation theory. Calculation of the ϕ's to a given degree of accuracy is much more laborious when this approximate analytical method is used than when the numerical method described below is used. Therefore, further details of this analytical method will be omitted.

Another type of analytic approximation results from allowing the variable n, originally defined as discrete, to take on continuous values. This procedure was followed by Zeldovich[7] in treating the simple steady-state situation. If a(n), b(n), and $\phi(n, \tau)$ are any functions of the continuous variable n $(2 \leq n < \infty)$ which take on the values a_n, b_n and $\phi_n(\tau)$ defined by Eqs. (100), (101) and (11), respectively, when n is an integer, and if $\phi(n, \tau)$ also possesses partial derivatives of all orders with respect to n, then

$$\phi(n \pm 1, \tau) = \phi(n,\tau) \pm \frac{\partial \phi(n,\tau)}{\partial n} + \frac{1}{2!} \frac{\partial^2 \phi(n,\tau)}{\partial n^2} \pm \cdots \qquad (105)$$

so that Eq. (100) can be written

$$\frac{\partial \phi(n,\tau)}{\partial \tau} = [a(n) + b(n)] \left[\frac{1}{2!} \frac{\partial^2 \phi}{\partial n^2} + \frac{1}{4!} \frac{\partial^4 \phi}{\partial n^4} + \cdots \right]$$

$$+ [a(n) - b(n)] \left[\frac{\partial \phi}{\partial n} + \frac{1}{3!} \frac{\partial^3 \phi}{\partial n^3} + \cdots \right] . \qquad (106)$$

In order to reduce Eq. (106) to tractable form, it is necessary to make some assumption about the magnitude of the higher derivatives. In several direct numerical integrations of Eq. (100) which have been carried out (see below), it has been found that, through most of the range of n and τ , the quantities ϕ_n behave approximately like a decreasing geometric series with a ratio between 1/2 and 1/4. It follows that $\phi(n, \tau)$ is roughly proportional to e^{-n}, and therefore all the derivatives with respect to n are approximately of the same magnitude. Equation (106) can then be approximated by

$$\frac{\partial \phi}{\partial \tau} = \frac{1}{2} (a + b) \frac{\partial^2 \phi}{\partial n^2} + (a - b) \frac{\partial \phi}{\partial n} \qquad (107)$$

with an error of the order of 10%.

Equation (107), as it stands, represents no significant simplification of the original Eq. (100), because the functional form of b(n) is too complicated to permit finding an analytic solution. The first step in obtaining a numerical solution, on the other hand, is to approximate the continuous variable n by a discrete variable, which can best be done by use of Eq. (100) rather than Eq. (107). The only region where Eq. (107) appears to be useful is in the region near the critical size where R_n has a maximum, so that $R_{n-1} \approx R_n$. Then, $a(n) \approx b(n)$ by Eqs. (101) and (102a); also $a(n_*) = \beta_{1,n_*} \approx n_*^{2/3}$, so that Eq. (107) becomes

$$\frac{\partial \phi}{\partial \tau} \approx n_*^{2/3} \frac{\partial^2 \phi}{\partial n^2} \qquad \text{(near critical n).} \qquad (108)$$

It is seen from the dimensional form of Eq. (108) that any characteristic condensation time, τ, which happens to be determined mainly by the growth processes in the neighborhood of the critical size, should be proportional to $n_*^{4/3}$. Moreover, a solution to Eq. (108) with the boundary conditions $\phi(1,\tau) = 1$, $\phi(n,0) = 0$ can be obtained immediately by comparison with the equivalent heat-conduction problem;[25] it is

$$\phi(n,\tau) \approx 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{1}{2} m n_*^{-1/3} \tau^{-1/2}} e^{-x^2} dx. \qquad (109)$$

According to Eq. (109), $\phi(n_*, \tau)$ at the critical size will reach a value of 0.5, which is approximately its steady-state value, at a time $\tau = 1.1\, n_*^{4/3}$. This result is likely to be a poor approximation because of the boundary condition applied to Eq. (108) at the point $n = 1$ where the neglected terms are large. An equation similar to Eq. (109) has recently been obtained by Kantrowitz.[26]

In order to obtain a reasonably accurate picture of the variation of the ϕ's with time, it appears necessary to integrate Eq. (100) numerically. Since the values of many of the ϕ's increase by eight to ten orders of magnitude during the time period of interest, and since the earlier small values cannot be neglected because they affect the smaller ϕ's corresponding to larger values of n significantly, many conventional methods of numerical integration prove exceedingly slow. After considerable experimentation, a combined numerical and graphical method has been developed which permits relatively rapid integration of the equations with reasonable accuracy. Equation (100) is first transformed to

$$\frac{d \log \phi_n}{d\tau} = a_n\left(\frac{\phi_{n+1}}{\phi_n} - 1\right) + b_n\left(\frac{\phi_{n-1}}{\phi_n} - 1\right). \qquad (110)$$

The values of ϕ_n are plotted against τ on semilogarithmic paper having many cycles, to cover the full variation of the ϕ's; a second strip of semilogarithmic paper is used as a scale to measure distances between the ϕ's. The combination acts like a slide rule, and by simply decreasing the numbers on the scale by unity the values of $(\phi_{n+1}/\phi_n - 1)$ and $(\phi_{n-1}/\phi_n - 1)$ can be read directly. The logarithmic derivatives of the ϕ's can then be calculated numerically from Eq. (110), and any of several well-known numerical integration methods used to complete the step-by-step integration. Further details are given in a later section. Relatively large time intervals can be used since the logarithms of the ϕ's are found to vary nearly linearly with τ.

Certain qualitative properties of nonsteady solutions of the condensation equations can be deduced without the difficulties which accompany a quantitative treatment. Such properties not only provide a general picture of the condensation process but also serve to guide and check the numerical integrations. One property concerns the role played by the steady-state ϕ's discussed in section 2.10. These quantities, which will be denoted by $(\phi_n)_s$ in the present discussion, decrease gradually with increasing n from a value of unity at $n = 1$ to a value of approximately one-half at the critical n. This last statement follows readily from the electrical analogy since the large resistances R_n are distributed nearly equally on either side of the critical n. The steady-state values satisfy Eq. (100) when the time derivative is equated to zero:

$$0 = a_n (\phi_{n+1})_s - (a_n + b_n)(\phi_n)_s + b_n(\phi_{n-1})_s \qquad (111)$$

If this equation is subtracted from Eq. (100), one obtains

$$\frac{d\phi_n}{d\tau} = a_n\left[\phi_{n+1} - (\phi_{n+1})_s\right] - (a_n + b_n)\left[\phi_n - (\phi_n)_s\right] + b_n\left[\phi_{n-1} - (\phi_{n-1})_s\right]. \qquad (112)$$

The initial values, $\phi_n(0)$, for the nonsteady situation decrease rapidly with increasing n and generally become negligible for $n > 10$, as has already been pointed out. Therefore, all of the $\phi_n(\tau)$ are initially less than the corresponding $(\phi_n)_s$. It follows from Eq. (112) that no $\phi_n(\tau)$ can exceed the corresponding $(\phi_n)_s$ at any later time. The first $\phi_n(\tau)$ which might reach $(\phi_n)_s$ must have at this instant a negative time derivative since the first and third terms on the right hand side of Eq. (112) are negative and the middle term vanishes. In the exceptional case that ϕ_n is surrounded by several ϕ's, all of which reach their steady-state values simultaneously, this simple argument is not applicable because $d\phi_n/d\tau$ becomes zero. However, it can be shown by repeated differentiation of Eq. (112) and use of Eqs. (100) and (111) that the first nonzero derivative of $\phi_n(\tau)$ is negative, so that the theorem still holds.

In general, $\phi_{n-1}(0)$ is much greater than $\phi_n(0)$. When n is less than n_*, then a_n is less than b_n. It follows from Eq. (100) that $d\phi_n(0)/d\tau > 0$ for $n < n_*$, while usually $d\phi_n(0)/d\tau \approx 0$ when $n \geq n_*$ because all the $\phi_n(0)$ are negligible when $n > 10$. If Eq. (100) is differentiated to give

$$\frac{d^2\phi_n}{d\tau^2} = a_n \frac{d\phi_{n+1}}{d\tau} - (a_n + b_n)\frac{d\phi_n}{d\tau} + b_n \frac{d\phi_{n-1}}{d\tau}, \tag{113}$$

an argument similar to that used with Eq. (112) shows that the derivatives $d\phi_n/d\tau$ can never become negative. The details will not be given here. It follows from this result and the result obtained in the preceding paragraph that the $\phi_n(\tau)$ at any particular time must form a decreasing series in n, because Eq. (100) can be written

$$\frac{d\phi_n}{d\tau} = a_n(\phi_{n+1} - \phi_n) - b_n(\phi_n - \phi_{n-1}), \tag{114}$$

and, therefore, if ϕ_{n-1} were less than ϕ_n and $d\phi_n/d\tau \geq 0$, ϕ_n would have to be less than ϕ_{n+1}. Repeating the argument, one obtains $\phi_{n+1} < \phi_{n+2} < \phi_{n+3} < \ldots$, which is impossible since

$$\lim_{n\to\infty} \phi_n \leq \lim_{n\to\infty} (\phi_n)_s = 0.$$

These various results can be summarized in the following statement: At all times the quantities $\phi_n(\tau)$ form a decreasing series in n; each of these quantities increases steadily with time to approach asymptotically the corresponding steady-state value as an upper limit.[*] The numerical integrations which have been carried out not only confirm this behavior, but also show that the values of the ϕ's increase with time almost as if a voltage wave with a rather sharp front were passing down the electrical circuit in the direction of increasing n. The time required for the formation of observable macroscopic droplets can then be approximated by the time required for the ϕ_n in the neighborhood of the critical size to reach essentially their steady-state values, plus the time required for the steady-state J to "fill up the pipeline" between the critical size and the observable macroscopic size. The first-named time period appears to be generally 1/10 to 1/100 of the value given by the very approximate Eq. (109), and is usually less than a microsecond. This time period is entirely negligible in most physical situations. The second time period mentioned above can be calculated directly from Eq. (96a); it is simply

$$
\begin{aligned}
(t)_{delay} &= J^{-1} \sum_{n=n_*}^{n_o} (N_n)_s \\
&= V \sum_{n=n_*}^{n_o} N_1^{\,n} \exp\left(-\frac{F_n^\circ - nF_1^\circ}{kT}\right) \sum_{i=n}^{\infty} R_i ,
\end{aligned}
\tag{115}
$$

where n_o is the observable size. This latter time delay is usually of the order of 10^{-4} to 10^{-6} seconds. In some physical situations this

---

[*] The mathematical proof that each $(\phi_n)_s$ is actually the asymptote of $\phi_n(\tau)$ is a rather lengthy one and will not be given here.

time delay is negligible, so that the Becker-Döring steady-state approximation is quite accurate. In other physical situations, where such a time period is important, it can be readily computed from Eq. (115) without the complications of a numerical integration.

2.12. The Effects of Admixtures and Impurities

The analysis presented thus far has been directed toward the condensation process in a pure vapor. By modifying the expressions for some of the parameters, however, the analysis can be applied to many situations in which other materials are mixed with the vapor.

The simplest situation occurs when the vapor is mixed with an inert gas which is virtually insoluble in the corresponding liquid. To a good approximation, such an admixture does not effect the early stages of condensation. The pressure of the gas on the droplets is generally negligible compared to the "surface-tension pressure," $2\sigma/r$, for droplets of molecular size. Only when the droplets grow to many times critical size should this effect and the effect of vapor concentration gradients in the gas mixture become important.

When the vapor is mixed with a soluble gas, the larger droplets will contain gas molecules in solution. The equilibrium concentration of dissolved gas as a function of droplet size can be computed from the thermodynamics of two-component, two-phase systems (see Gibbs[18]). In general, the gas concentration decreases with decreased droplet size, so that the effect of the gas on the vapor condensation will be small unless the gas is very soluble. In the latter case, the free energies of droplets having the equilibrium composition can be simply substituted into the condensation equations, and the remainder of the analysis carried out as before.

A more significant effect on the condensation may occur when the vapor contains suspended liquid or solid particles. If these particles are wetted by the condensed vapor, they may initiate condensation at much lower saturation ratios than would otherwise be required. In principle, the condensation theory developed previously can be applied to condensation around such particles by using modified β_{ij}'s and modified free energies. The β_{ij}'s would be based on the effective vapor-molecule capture cross section of the particles, and the free energies would be calculated from the particle size and shape, and the three pertinent surface tensions (particle-vapor, particle-liquid, and vapor-liquid). Probably the calculated condensation process would depend greatly on the exact size and shape assumed for the particles, and especially on whether cracks and crevices are assumed. Many different numerical calculations for different cases might have to be carried out before any general results of physical significance could be stated with assurance. Such calculations have not been attempted in the present investigation.

As is well known, ions can also serve to nucleate condensation. If each ion has a radius a and charge e, and is assumed to be situated at the center of a droplet, the free energy given by Eq. (55) should, to a first approximation, be increased by the quantity[12]

$$\frac{e^2}{2}\left(1-\frac{1}{K_e}\right)\left[\left(\frac{4\pi\rho_L}{3m}\right)^{1/3} n^{-1/3}-\frac{1}{a}\right]$$

where K_e is the dielectric constant of the liquid. For a second approximation, the increase of droplet radius due to the volume of the ion should also be taken into account. The various condensation parameters can then be evaluated and numerical calculations made. Such analysis will not be included here.

III. THEORY OF VAPORIZATION (BUBBLE FORMATION)

3.1. Preliminary Considerations

When a liquid under a positive pressure is heated to a sufficiently high temperature the liquid boils, that is, small vapor bubbles are formed which grow rapidly in size at the expense of the liquid. The similarity between this process and the converse condensation process is evident. When a liquid is placed under tension, it ruptures or cavitates. The similarity in this case is not so complete because the vapor phase may play little or no part in the rupture.

The development of a precise theory of vaporization is more difficult than the similar development for condensation, essentially for the reason that the kinetic theory of liquids is more difficult than the kinetic theory of gases. With the help of a number of approximations and simplifying assumptions, however, a rather crude theory of vaporization can be developed which may be sufficient to answer certain practical questions.

A vapor bubble or cavity in a liquid might be characterized by its size and shape, the amount of vapor it contains, and the temperature of the vapor. As was observed in the condensation case, the development of a simple theory becomes possible only if these four variables can be reduced to a single independent variable. The shape parameter can be eliminated by the assumption that all bubbles are spherical. For large bubbles, this assumption is probably a good approximation. The smallest bubbles and cavities, however, are probably more like irregular cracks and fissures between the molecules (see Frenkel,[12] p. 177) so that the use of the assumption for these cavities is justifiable only because the calculated vaporization process is not greatly affected by considerable errors in the treatment of the very smallest bubbles.

The temperature of the vapor in the bubble can probably be equated to the liquid temperature with small error, because the vapor coming from a liquid has the same temperature as the liquid (only the more energetic molecules are able to escape, which effect exactly compensates for the latent heat of vaporization). Such evaporation, to be sure, cools the liquid surrounding the bubble; but bubbles of interest are so small that heat conduction in the liquid should act rapidly enough to remove any significant temperature differences in such small regions.

There remain the two variables of bubble size and vapor mass, one of which must be eliminated. In the case of boiling at appreciable positive pressure, the rate-determining process is probably the transfer of molecules from the liquid to the vapor phase; thus, the important parameter is the amount of vapor in a bubble, while its size on the other hand can be approximated by the condition for mechanical equilibrium, following Döring.[6] In the case of cavitation, or rupture at small or negative pressures, the rate-determining process is probably the separation of liquid molecules to leave a hole so that the important parameter is the cavity size, while the amount of vapor it contains can either be estimated from the vapor pressure of the liquid, or entirely neglected, as was done by Zeldovich[8] and Fisher.[10]

3.2. The Basic Equations for Boiling (Positive Pressures)

If a spherical vapor bubble of radius r_n contains n vapor molecules at a pressure p_n and temperature T, the perfect gas relation gives

$$\frac{4}{3}\pi r_n^3 p_n = nkT . \tag{116}$$

If the droplet radius is estimated from the condition of mechanical equilibrium, one obtains

$$\frac{2\sigma}{r_n} = p_n - p_\infty , \tag{117}$$

where p_∞ is the pressure in the liquid, which also equals the pressure of the vapor in a bubble of infinite size in mechanical equilibrium. Either p_n or r_n can be eliminated from Eqs. (116) and (117) to give, respectively,

$$r_n^3 + \left(\frac{2\sigma}{p_\infty}\right)^2 r_n^2 = \left(\frac{3kT}{4\pi p_\infty}\right) n ; \tag{118}$$

$$\frac{p_n}{(p_n - p_\infty)^3} = \left(\frac{3kT}{32\pi\sigma^3}\right) n . \tag{119}$$

These equations give r_n and p_n as implicit functions of n. Because the conditions of sphericity and mechanical equilibrium are only roughly satisfied when n is small, the introduction of Tolman's correction to the surface tension for small radii of curvature is not warranted.

The rate at which the vapor molecules strike the bubble wall is, from simple kinetic theory, $2(2\pi/mkT)^{1/2} r_n^{\;2} p_n$. If a fraction α_n of these are captured by the liquid, then

$$\text{Rate of condensation of vapor molecules on the bubble wall} = 2\left(\frac{2\pi}{mkT}\right)^{1/2} \alpha_n r_n^{\;2} p_n . \tag{120}$$

If p_n were varied until it equaled the vapor pressure, P(T), of the liquid,* the rate of condensation of vapor molecules would equal the rate of vaporization of liquid molecules from the bubble wall. It follows that

$$\text{Rate of vaporization of liquid molecules from the bubble wall} = 2\left(\frac{2\pi}{mkT}\right)^{1/2} \alpha_n r_n^2 P. \tag{121}$$

The vapor pressure, P, of the liquid is a function of the temperature and pressure in the liquid phase, and is the same for bubbles of all sizes, independent of their surface curvature (see the errata to Döring's paper).[6]** In the boiling situation under consideration, the difference between the pressure on the liquid and the vapor pressure of the liquid is seldom more than a few atmospheres. Therefore, the ratio of P to the ordinary vapor pressure, which ratio can be obtained from the Gibbs-Thomson relation, Eq. (61), is so near unity that the difference can be neglected.

If N_n denotes the number of bubbles of size n per unit volume of liquid, N_n will be increased in time by the growth of bubbles from the next smallest size and shrinkage of bubbles from the next largest size, while it will be decreased by the converse processes. Evaluating the rates of these four processes with the help of Eqs. (120) and (121), one obtains

---

*Throughout the discussion, lower case p's are used for actual pressures existing in the liquid or vapor, and capital P's for vapor pressures which are properties of the liquid phase and may not correspond to the actual pressure of any phase present.

**The vapor pressure of small liquid droplets depends on their curvature only because the internal pressure in the liquid includes a term $2\sigma/r$.

$$\frac{dN_n}{dt} = 2\left(\frac{2\pi}{mkT}\right)^{1/2}\left(\alpha_{n-1} r_{n-1}^2 P N_{n-1} - \alpha_n r_n^2 p_n N_n - \alpha_n r_n^2 P N_n + \alpha_{n+1} r_{n+1}^2 p_{n+1} N_{n+1}\right), (n>1). \tag{122}$$

In comparison with Eq. (14a), for condensation, Eq. (122) lacks a volume-change term, since the liquid is assumed incompressible. Equation (122) also lacks nonlinear terms corresponding to the consolidation of two bubbles, or the splitting of one bubble into two. There is no simple way to derive such nonlinear terms, but, by analogy with the condensation case, it may be presumed that their contribution to the vaporization process is small.

An electrical analogy for the vaporization process may be obtained by defining

$$\phi_n(t) = \frac{\alpha_n}{\alpha_1}\left(\frac{r_n}{r_1}\right)^2 \frac{N_n}{N_1} \prod_{i=2}^{n}\left(\frac{p_i}{P}\right);\ \phi_1(t) = 1; \tag{123}$$

$$C_n(t) = \frac{\alpha_1}{\alpha_n}\left(\frac{r_1}{r_n}\right)^2 N_1 \prod_{i=2}^{n}\left(\frac{P}{p_i}\right); \tag{124}$$

$$R_n(t) = \frac{1}{2}\left(\frac{mkT}{2\pi}\right)^{1/2}\left(\alpha_1 r_1^2 N_1 P\right)^{-1} \prod_{i=2}^{n}\left(\frac{p_i}{P}\right). \tag{125}$$

In terms of these variables, Eq. (122) becomes

$$\frac{d(C_n\phi_n)}{dt} = \frac{\phi_{n-1} - \phi_n}{R_{n-1}} - \frac{\phi_n - \phi_{n-1}}{R_n}, \ (n>1), \tag{126}$$

which is identical with Eq. (15), so that the electrical circuit of Fig. 1 is again obtained, with somewhat different values for the circuit parameters.

3.3. The Equilibrium Solution of the Vaporization Equations

As in the condensation case, the equilibrium bubble distribution corresponds to $\phi_n = 1$ for all n. In view of Eq. (123), this condition becomes

$$N_n = \frac{\alpha_1}{\alpha_n}\left(\frac{r_1}{r_n}\right)^2 N_1 \prod_{i=2}^{n}\left(\frac{p}{p_i}\right). \tag{127}$$

In most cases one can probably set $\alpha_1 \approx \alpha_n \approx 1$ (see the discussion on accommodation coefficients in section 2.3). The r's and p's in Eq. (127) can be evaluated from Eqs. (118) and (119). There remains the problem of evaluating N_1, the equilibrium number of bubbles containing one vapor molecule. To obtain a value, probably correct to within an order of one or two magnitudes, Döring[6] simply equated N_1 to the number of liquid molecules which have a kinetic energy at least sufficient to remove a molecule from the interior of the liquid and leave a hole. A more exact value of N_1 might be obtained from free-energy considerations. In view of the approximations involved in the concept of a "one-molecule vapor bubble," such a refinement does not appear to be warranted.

3.4. The Steady-State Solution

By analogy with the similar condensation process, the constant rate of formation of bubbles in the steady-state situation is

$$J = \frac{1}{\sum_{n=1}^{\infty} R_n}. \tag{128}$$

By approximating summations by integrals and making other simplifications, Döring[6] found that

$$J \approx N_L^{4/3}\left(\frac{6e_{vap}}{m}\right)^{1/2} exp\left(-\frac{16\pi\sigma^3}{3kT(P-p_\infty)^2}-\frac{2e_{vap}}{kT}\right), \qquad (129)$$

where N_L is the number of liquid molecules per unit volume and e_{vap} is the energy of vaporization per molecule.

Because of the approximations inherent in the whole method of approach, no attempt has been made by the writer to improve the details of Döring's analysis for the steady state.

3.5. Time-Dependent Solutions of the Vaporization Equations

As in the condensation case, the time-dependent vaporization equations can be solved by numerical integration. Calculations are most easily performed for situations where the liquid is suddenly heated or its pressure is suddenly reduced (or both), and thereafter the temperature and pressure are held constant. To treat such situations, it is convenient to introduce a dimensionless time:

$$\tau = 2\left(\frac{2\pi}{mkT}\right)^{1/2}\alpha_1 r_1^2\, Pt\,, \qquad (130)$$

and write Eq. (126) as

$$\frac{d\phi_n}{d\tau} = a_n\,\phi_{n+1} - (a_n + b_n)\phi_n + b_n\,\phi_{n-1}\,,\ (n>1)\,, \qquad (131)$$

where the quantities C_n and R_n have been combined into

$$a_n = \frac{\alpha_n}{\alpha_1}\left(\frac{r_n}{r_1}\right)^2; \qquad (132)$$

$$b_n = \frac{\alpha_n}{\alpha_1}\left(\frac{r_n}{r_1}\right)^2\left(\frac{p_n}{P}\right) . \qquad (133)$$

Equation (131) is identical to Eq. (100) for condensation, and the same numerical-graphical method can be used for its solution. Similarly, the characteristic way in which such solutions approach asymptotically the steady-state values is also found in this case. The critical size for the present problem is given by the condition $p_{n_*} = P$, whence $b_{n_*} = a_{n_*} \approx (p_1 n_*/P)^{2/3}$ from Eqs. (132), (133) and (116). By use of the same approximation as that involved in Eq. (109), it follows that the time required for the ϕ_n near the critical size to reach virtually their steady-state values is roughly $\tau \approx 1.1\,(p_1 n_*/P)^{4/3}$.

3.6. The Equations for Cavitation or Liquid Rupture (Negative Pressures)

If the vaporization equations developed in the last few sections are applied to the case of a liquid under tension, one difficulty immediately presents itself. Since p_∞ is negative, the left hand side of Eq. (118) has a minimum for a certain value of r_n, while the right hand side approaches $-\infty$ as n increases. Thus, for values of n beyond a certain point, n_{max}, there can exist no vapor bubbles in mechanical equilibrium. If it is assumed that bubbles which reach such a size automatically continue to grow and thus can be dropped from consideration, the boundary condition $\phi_{n_{max}+1} = 0$ can be applied. This assumption was used by Döring[6] to calculate the steady-state rate of cavitation:

$$J = N_L^{4/3}\left(\frac{6e_{vap}}{m}\right)^{1/2} \exp\left[-\frac{128\pi\sigma^3}{81kTz^2}\left(\log\frac{z}{P} + \frac{m(z+P)}{kT\rho_L} + \frac{3}{2} - \log 2\right) - \frac{2e_{vap}}{kT}\right] \tag{134}$$

where z is the absolute value of the tension on the liquid, P is the vapor pressure of the liquid at ordinary pressures, and the change in the actual vapor pressure due to the tension is now taken into account. For the nonsteady situation, the numerical integration of Eq. (131) can be carried out with the same boundary condition.

It is somewhat doubtful, however, whether such equations involving the number of vapor molecules as the chief parameter can satisfactorily represent cavitation or rupture under large tensions. As mentioned previously, the rupture process probably is determined by the rate at which liquid molecules can separate to form a hole, while the role of any vapor present is probably insignificant. In such cases, the theories of Zeldovich[8] or Fisher,[10] which neglect the vapor and consider only the cavity size, are probably more suitable. Zeldovich's theory gives the steady-state cavitation rate as a function of the liquid surface tension and viscosity, while Fisher uses the theory of absolute reaction rates to obtain the same quantity as a function of the surface tension and the free energy of activation for a molecule to move from one equilibrium position in the liquid lattice to another. A critical comparison and a further refinement of the two theories are highly desirable, but have not yet been carried out.

3.7. The Effect of Impurities on Vaporization

As is well known, impurities present in a liquid can greatly increase vaporization rates, and, in fact, prevent the attainment of significant superheating or tensile strength. The nucleating effect of a particle of impurity depends on its size, shape and the degree to which it is wetted. A bubble which starts to grow about an incompletely wetted particle will be bounded on one side by the surface of the particle and on the other side by a liquid surface which forms a portion of a sphere. The liquid surface meets the solid surface at an angle determined by the three relevant surface tensions (liquid-vapor, liquid-solid and solid-vapor). Thus, the radius of curvature, r_n, of the spherical portion of the bubble surface can be calculated as a function of n geometrically, and the result used to replace Eq. (116). Equation (117) remains valid, but the a_n in Eqs. (120) and (121) must be modified to allow for the change in the surface area of bubble which is in contact with the liquid. With these modifications in the values of the parameters, the basic differential equations for vaporization, Eqs. (126) and (131), remain valid, and numerical solutions can be obtained as before. Depending upon the exact size, shape and wettability assumed for the particles, one can obtain any limit for the superheating or tensile strength from zero up to the maximum values for a pure liquid. The practical application of such calculations requires the knowledge of what sizes and shapes of impurity particles are likely to be present in liquids of interest. In the absence of such information, one might attempt a large number of calculations for different types of impurity particles in the hope of obtaining some generally valid results.

IV. RESULTS AND DISCUSSION

4.1. Comparison of Free-Energy Values Given by Macroscopic Formulas with Reed's Numerical Values

The free-energy values for small nitrogen aggregates calculated by Reed[23] are compared with those given by the theoretical formulas of sections 2.7 and 2.8 in Figs. 2 and 3, for temperatures of 77.3°K and 96.6°K, respectively. The points at n = 6 and 8 include the effect of isomers (different aggregate configurations having the same number of molecular bonds), with a slight change from Reed's values to remove an apparent error in his allowance for isomers. The solid curves represent Eqs. (52), (54) and (65) with $\epsilon = 0$; i.e., with no allowance for the change of surface tension with radius. No value of ϵ for liquid nitrogen is available, and so a value of 0.5, which is typical of liquids of low molecular weight,[19] was used in the same three equations to yield the dashed curves.

Reed's values are seen to agree quite well with Eq. (54), based on the "volume expansion" method, and only slightly less well with Eq. (65), based on the Gibbs-Thomson equation. The agreement with Eq. (52), based on the partition functions, is poor. The curves which neglect the Tolman surface-tension correction lie closer to Reed's values than those which include the correction. Reed's value for n = 6 appear high compared to the general trend of the other values,* while

---

*Reed plotted log (P_n/P_∞) which depends upon $F_n^o - F_{n-1}^o$ by Eq. (58b). Thus, for n = 6 he obtained high values corresponding to the high values of $F_6^o - F_5^o$, while for n = 8 he obtained low values corresponding to the low values of $(F_8^o - F_6^o)/2$. The quantity which actually enters into the condensation equations, however, is $(F_n^o - nF_1^o)$ which depends upon the cumulative product of (P_n/P_∞), according to Eq. (59), and this quantity does not have a low value at n = 8.

his values for n = 8 are not relatively high. There is some reason for believing that, as n is increased beyond eight and the aggregate approaches the close-packed configuration of one molecule surrounded by twelve nearest neighbors, the increased number of molecular bonds may lower the free energy values close to the dashed curves which include the Tolman correction to the surface tension. This conjecture is far from certain, however, because several other factors besides the number of bonds affect the free energy. The data at hand are insufficient to determine whether use of the Tolman correction increases or decreases the accuracy of the condensation equations when the critical size is greater than eight.

It might seem from Figs. 2 and 3 that the total effect of the Tolman correction and some of the other discrepancies should be small. However, the free energy enters exponentially into the condensation relations so that a difference of only 4.6 units on the vertical coordinate of these graphs is equivalent to a factor of 100 in the condensation rates. Although the percentage difference between the alternative free-energy curves decreases as n increases, the numerical difference increases and thus produces a variation in the exponential function of many orders of magnitude when n is as large as 50 or 100.

4.2. Steady-State Rates of Condensation

An important parameter which determines the steady rate of droplet formation is the size, n_*, that corresponds to the maximum resistance parameter, R_{n_*}. As explained in section 2.10, n_* differs slightly from the critical size, n_c, except in the Becker-Döring approximation. Values of n_* for water vapor at 0° C and various saturation ratios are shown in Fig. 5. The three solid and three dashed curves correspond to the three alternative expressions for the free energy mentioned before. The considerable effect of the introduction of Tolman's correction to the surface tension is shown by the difference between the solid and the dashed curves. In all cases, the values of n_* decrease with increasing saturation ratio since a smaller droplet is stable relative to a more highly supersaturated vapor. The curves based on free-energy values given by Eqs. (54) and (65) lie quite close together, while the curves based on Eq. (52) lie considerably lower, corresponding to the lower free-energy values obtained under the latter assumption.

Values of the steady-state rate of condensation, J, corresponding to these values of n_* are plotted in Fig. 6. Six different curves are found, depending upon which expression for the free energy is used and whether Tolman's correction is included. A seventh curve, shown cross-hatched, represents Becker and Döring's[5] simplified expression for J. All of these curves are based on a value of $\beta_{1,n} = n^{2/3}$, which corresponds to values of the accommodation coefficient $\alpha_{1,n}$ slightly less than unity, as shown in Fig. 4. If $\alpha_{1,n}$ is unity, the values of J would be increased by factors of 1.2 to 2.8, but this factor is negligible for most considerations.

A very great increase of J with increase in the saturation ratio is characteristic of all the curves in Fig. 6. Considerable differences between the different curves representing different assumptions also appear. When the Tolman correction is omitted, the curves based on free energies given by Eqs. (54) and (65) lie quite close together, while the curve based on Eq. (52) lies much higher. The introduction of the Tolman correction raises all of the curves considerably. The fairly small difference between the curve based on Eq. (65) with $\epsilon = 0$ and the Becker-Döring curve is due to factors which Becker and Döring dropped in their approximate calculation.

Powell,[27] using an expansion chamber, found experimentally that water vapor at 0° C first condensed into a cloud of microscopic droplets at a saturation ratio of 5.40. If, after condensation, the vapor is saturated and at a temperature near 0° C, approximately 7×10^{17} water molecules per cm^3 must have condensed. In the steady state at this saturation ratio only about 10^2 droplets per cm^3 of each size n can exist when n is larger than about 100 (see Fig. 9). Therefore, there should be about 10^{10} droplets of average size $n = 5 \times 10^7$ in the condensed vapor. For observation times of the order of a second, this value corresponds to $J = 10^{10}$. The latter figure is in satisfactory agreement with the curves corresponding to Eqs. (54) and (65) when the Tolman correction is omitted. When the correction is included, much higher theoretical values of J are obtained. It is possible, however, that the heating effect during the droplet growth process, which has been neglected in the present analysis, will act to decrease the theoretical values of J sufficiently to give agreement between experiment and theory when the Tolman correction is included rather than omitted.

The third pair of curves, corresponding to Eq. (52), gives much too high values of J both with and without the Tolman correction. This disagreement corresponds to the disagreement of Eq. (52) with Reed's free energy values discussed previously. Therefore, it seems evident that Eq. (52), based on the translational and rotational partition functions for a rigid sphere, gives erroneous free-energy values.

4.3. Computational Method for the Nonsteady Condensation Process

Considerable effort has been devoted toward the development of a practical method of solving the linearized time-dependent condensation equations numerically. The method finally worked out is illustrated in Fig. 7. The points A, B, C and D represent values of ϕ_n at time τ = 0.50 for four consecutive values of n which have been chosen to illustrate the method. The logarithmic scale shown in the insert is marked on a separate slip of paper. When the zero is placed at the point C, the reading at point B gives the value of $\phi_{17}/\phi_{18} - 1$ and the reading at D gives $\phi_{19}/\phi_{18} - 1$ since the two logarithmic scales act like a slide rule and the scale markings are decreased by unity from their ordinary values. The quantities read from the scale are then multiplied by b_n and a_n, respectively, and added to give the logarithmic derivative of ϕ_{18}, according to Eq. (110). With the help of the slope scale, the straight line CE is then constructed with this value of the slope. Similar constructions are carried out for adjacent values of n. The scale measurements and slope calculations are now repeated using the endpoints of the line segments at $\tau = 0.60$. The new slope is used to construct the line FG which starts at the midpoint of CE. Slope calculations are repeated at $\tau = 0.60$ and lines are drawn from the point F until the process finally converges on the line FH. The convergence can be speeded by judicious guesses.

In the integration process described above, the change of each ϕ_n over the unit interval is effectively approximated by the magnitude of the interval multiplied by the mean of the slopes at the beginning and end of the interval. The curve for each ϕ_n is thus extended from its initial value, given by Eq. (98b), to the point where it becomes essentially equal to its asymptotic value, $(\phi_n)_s$, given by Eq. (95b). The computational graphs cover the range from $\phi_n = 1$ down to $\phi_n = 10^{-10}$ or 10^{-12}, below which value ϕ_n and N_n are negligible. As the computation proceeds, new curves for larger values of n are started at the bottom of the graphs by simple extrapolation. This procedure can be shown to lead to negligible error. In regions where the ϕ's are still considerably less than their asymptotic values, it is found that the curves for successive values of n are quite evenly spaced. Therefore, the computational labor can be halved by omitting every other curve and expanding the measuring scale by a factor of two to allow for this omission. As the ϕ's approach their asymptotes, the intermediate curves can be introduced halfway between the other curves, and their subsequent behavior computed in detail.

4.4. Results for the Nonsteady Condensation Process

Figures 8a and b, 9 and 10 show the growth of droplets in water vapor at 0° C when the saturation ratio is 4, 6 and 8, respectively. The number of droplets shown at t = 0 corresponds to the assumption that the vapor was originally saturated at temperatures of 27.0, 35.8 and 42.6° C, and then expanded adiabatically to 0° C so rapidly that the droplets do not have time to grow during the expansion. These initial temperature values were chosen so as to give the desired saturation ratios at 0° C. In all of the droplet growth calculations the simple values of a_n and b_n given by Eqs. (103) and (104ab) are used. These values are based on free energies obtained in Eq. (65) by the use of the Gibbs-Thomson equation. The results, however, would be only slightly changed if Eq. (54) were used for the free-energy values instead of Eq. (65).

Figures 8a and 8b, for a saturation ratio of four, show the rapid rate at which the number of very small droplets approaches the steady-state value. Since the time required for these N_n to reach essentially their asymptotic values is short compared to the time required for the critical droplets, at $n = 90$, to reach equilibrium, a considerable variation in the accommodation coefficients, free energies or initial N_n values assumed for the droplets of smallest size will not affect the over-all condensation process significantly. Although the curves for larger n values and later times are less steep, the quantities N_n in the critical region still reach their steady-state values in a fraction of a microsecond. This time is negligible in practically all physical situations. A considerably longer time is required for droplets to grow from critical to macroscopic size, or for an appreciable amount of the vapor to condense. According to Fig. 8a, there will never be more than 10^{-7} droplets per cm^3 of a given size $n > 112$. In a volume of the order of a few cm^3 this cannot be strictly true, but it should be true on the average. Since J for this situation is about ten, in 10^3 seconds 10^4 droplets larger than critical size will be formed per cm^3. If there are an average of 10^{-7} droplets per cm^3 for each value of n from 112 to n_{max}, it follows that $n_{max} = 10^{11}$ molecules, corresponding to a radius of 10^{-4} cm. The average size of the 10^4 droplets is about 5×10^{10} molecules, so that in one second approximately 5×10^{14} vapor molecules have condensed, which is only a small fraction of the 6×10^{17} vapor molecules present.

Figures 9 and 10, for the higher saturation ratios of six and eight, respectively, exhibit droplet growth curves similar to those of Figs. 8a and 8b. The rate of droplet growth increases and the critical size decreases as the saturation ratio is increased so that the characteristic time intervals are somewhat shortened. The number of droplets of a given size in the steady state increases with the saturation ratio.

In Fig. 11, the actual times, t, and the dimensionless times, τ, for the critical size droplets to reach their steady-state number are plotted and compared with the times given by the very approximate relation $\tau \approx 1.1\, n_*^{4/3}$ derived from Eq. (109). The actual times are seen to be only 1/50 to 1/25 as great as those given by the simple formula. The exact values are fairly well represented in this range by the dashed lines which correspond to the formulas $\tau = 0.27\, n_*^{0.8}$ and $t = 1.1 \times 10^{-9}\, n_*^{1.7}$ sec.

In order to get an estimate of the magnitude of the nonlinear terms in the condensation equation which are neglected in most of the analysis, values of the initial $\phi_n(0)$ and also of the final asymptotic $(\phi_n)_s$ for water vapor at 0° C and a saturation ratio of four have been substituted into the nonlinear terms of Eq. (14a) and compared with the largest linear term, $(\phi_{n-1} - \phi_n)/R_{n-1}$. The ratios are presented in Table 1. This table shows that for very small n the nonlinear terms make a considerable contribution, but when n exceeds ten the nonlinear terms decrease to only a few percent. As long as the critical size is larger than about twenty, the nonlinear terms will have only a small effect. The apparent irregularities in the tabulated values are explained by the facts that droplets of size n = 2 and 3 cannot be formed by consolidation of two polymolecular droplets so that only negative nonlinear terms occur in these cases, while for larger n the even values of n have relatively more positive nonlinear terms than the odd values of n.

4.5. Results for the Nonsteady Vaporization Process

Figure 12 shows the growth of bubbles in water at 20° C which is suddenly subjected to a tension of 1000 atm. The calculations were carried out in the same fashion as those for the condensation situation. In this vaporization case, values of $\phi_n(t)$ rather than $N_n(t)$ are plotted because the N's vary so greatly with n that a scale which included them all would make their variation with time imperceptible. The behavior of each ϕ_n is similar to that of the corresponding N_n since the two quantities are proportional. The variation of the ϕ's with time is somewhat different in this situation than in the condensation situation primarily because the initial values $\phi_n(0)$ lie partially above and partially below the asymptotic steady-state values. Thus, many of the curves approach their asymptotes in an oscillatory fashion rather than monotonically as in the condensation case. Another difference is that there are no curves for $n > 46$, since bubbles of such size cannot exist at all in mechanical equilibrium (see section 3.6). As shown by Fig. 12, the calculations have not been extended to the attainment of the steady state, but only far enough to show that the steady state will be reached in approximately 3×10^{-12} seconds, a time entirely negligible for virtually all practical purposes. These calculations are for a tension of 1000 atm., in which situation the steady rate of bubble formation has the very small value of about 10^{-200} bubbles/(cm^3 sec). At a somewhat higher tension, where the bubble-formation rate becomes large, the time required for the attainment of the steady state is even shorter than 3×10^{-12} seconds.

Detailed calculations for rates of bubble formation in superheated water at positive pressure have not been carried out. However, by comparing the relevant coefficients with those for previous situations, one finds that in water at 1 atm. and about 295° C (the theoretical limit of superheating) the bubble formation should approach a steady rate in less than 10^{-10} seconds.

REFERENCES

1. M. Volmer and A. Weber, Z. phys. Chem. (1926), 119, 277.
2. M. Volmer, Kinetik der Phasentbildung, T. Steinkopff, Dresden and Leipzig, 1937.
3. L. Farkas, Z. phys. Chem. (1927), 125, 236.
4. R. Kaischew and I. N. Stranski, Z. phys. Chem. (1934), B-26, 317; Phys. Z. (1935), 36, 393.
5. R. Becker and W. Döring, Ann. der Phys. (1935), V-24, 719.
6. W. Döring, Z. phys. Chem. (1937), B-36, 371; (1938), B-37, 292.
7. J. Zeldovich, Zh. Exp. Theor. Fiz. (1942), 12, 525, (summarized in Ref. 12).
8. J. Zeldovich, Acta Physicochimica U.S.S.R. (1943), 18, 1.
9. D. Turnbull and J. C. Fisher, J. Chem. Phys. (1949), 17, 71.
10. J. C. Fisher, J. App. Phys. (1948), 19, 1062.
11. J. Frenkel, J. of Phys. (1939), 1, 315.
12. J. Frenkel, Kinetic Theory of Liquids, Oxford Univ. Press, 1946.
13. W. E. Hazen, Rev. Sci. Inst. (1942), 13, 247.
14. E. O. Barrett and L. S. Germain, Rev. Sci. Inst. (1947), 18, 84.
15. P. S. Epstein, Textbook of Thermodynamics, J. Wiley and Sons, N. Y., 1937.
16. R. C. Tolman, J. Chem. Phys. (1949), 17, 333.
17. F. B. Buff and J. G. Kirkwood, J. Chem. Phys. (1950), 18, 991.
18. J. W. Gibbs, Collected Works, Vol. I, Longmans, Green and Co., N. Y., 1928.
19. R. C. Tolman, J. Chem. Phys. (1949), 17, 118.
20. V. K. La Mer and G. M. Pound, J. Chem. Phys. (1949), 17, 1337.
21. R. M. Head, "Investigations of Spontaneous Condensation Phenomena, Thesis, Calif. Institute of Tech., 1949.

22. H. G. Stever and K. C. Rathbun, "Theoretical and Experimental Investigation of the Condensation of Air in Hypersonic Wind Tunnels," Aero. Eng. Dept., M.I.T., Oct. 1950.

23. S. G. Reed, Jr., "On the Early Stages of Condensation," Dissertation, Catholic Univ., 1951.

24. E. Jahnke and F. Emde, Tables of Functions, Dover Pub., N. Y., 1943.

25. H. S. Carslaw and J. C. Jaeger, Operational Methods in Applied Mathematics, Oxford Univ. Press, 1941.

26. A. Kantrowitz, "Nucleation in Very Rapid Vapor Expansions," Contributed Paper, Div. of Fluid Dynamics, Amer. Phys. Soc. Meeting at Urbana, Ill., May 12-13, 1950.

27. C. F. Powell, Proc. Roy. Soc. London (1928), A119, 553.

28. R. H. Fowler, Statistical Mechanics, second edition, Cambridge Univ. Press, 1936.

APPENDIX 1

Thermal Gradients Inside of Droplets

One of the approximations made in the course of the condensation analysis comes from the assumption that any nonequilibrium distribution of the energy among the various parts of a droplet, i.e., any internal temperature variation, is negligible. This assumption is plausible from a crude molecular viewpoint. The oscillatory velocities of the molecules in a liquid droplet and the translational velocities of the molecules in the vapor are comparable. The molecules in a droplet, however, are in a much denser state so that the kinetic energy imparted to a droplet by a colliding vapor molecule should be quite uniformly distributed over all the droplet molecules before the next collision occurs. There is a corresponding macroscopic argument. Consider water vapor at 0° C and four times the saturation pressure. Approximately 10^{22} vapor molecules strike a square centimeter of surface per second. These molecules contribute a latent heat of roughly 200 calories/(cm^2 sec) if all of them condense. Using the thermal conductivity of water, one obtains about 2×10^4 degrees/cm for the temperature gradient at the droplet surface. If the droplet radius is less than 10^{-6} cm (equivalent to about 10^5 molecules), the maximum temperature difference in the droplet is less than 0.02° C.

APPENDIX 2

Velocity Distributions of Particles Undergoing Elastic and Inelastic Collisions

It is a well-known result of kinetic theory* that in any system of particles which undergo purely elastic collisions the particle velocities tend toward the Maxwellian distribution:

$$N(M,u)du = \left(\frac{2}{\pi}\right)^{1/2}\left(\frac{M}{kT}\right)^{3/2} N(M)\exp\left(-\frac{Mu^2}{2kT}\right)u^2 du, \qquad (135)$$

where $N(M,u)\,du$ is the number of particles of mass M having velocities between u and du, and N(M) is the total number of particles of such mass.

Systems of particles undergoing inelastic collisions with resulting capture, such as in a droplet-vapor mixture, are more difficult to treat because the particles are then not in equilibrium. Useful results can be obtained, however, by mathematical induction. In a mixture of particles of mass M_1 and particles of mass M_2, both having Maxwellian velocity distributions, the probability of collisions for which the velocity of the center of mass of the two colliding particles lies between u and u + du is found from kinetic theory to be proportional to $\exp\left[-(M_1 + M_2)u^2/2kT\right]u^2\,du$. If the two particles stick together, it follows that the resulting aggregate will have a Maxwellian velocity distribution corresponding to its new mass.

---

*See, for example, Fowler.[28]

The result described above can be applied to each step in the growth of droplets from vapor molecules. It follows that the velocities of the droplets should be Maxwellian. One effect, however, has been ignored. After droplets of a given size have been formed, the ones with higher velocities are more likely to capture further vapor molecules, so that the mean velocities of the droplets remaining at the given size is slightly lowered. This effect is very small in condensation processes of interest, since the number of droplets of size n is always much greater than those of size n + 1 when n is smaller than the critical size. When n is larger than the critical size, the velocities of the droplets are negligible, so that it makes little difference whether they are Maxwellian or not.

APPENDIX 3

Equations for the Solution of the Nonisothermal Droplet-Growth Problem by a Monte Carlo Method

The name "Monte Carlo" is applied to the systematic replacement of physical or mathematical problems by equivalent "games of chance." With the help of a set of random numbers or other random device, the games of chance are then played a sufficient number of times to reduce the probable error of the averaged results to a sufficiently small value. The application of this method is quite obvious in physical problems which involve a large number of stochastic individual processes, as in all generalized diffusion problems, including the droplet growth problem. In the Monte Carlo method, the accuracy of the results increases with the number of individual calculations, and generally a large number of calculations are required to obtain reasonably reliable results. The accuracy is not affected by the number of independent variables in the problem so that the method is particularly useful in multidimensional problems where conventional numerical-integration methods are exceedingly lengthy.

In order to apply the Monte Carlo method to droplet growth, with allowance for the heating of the droplets as they grow, expressions must be derived for the probability of a given droplet growing or shrinking with a gain or loss of a given amount of energy, and the rate of occurrence of such changes must also be known. The problem is considerably simplified if it is assumed that each droplet grows independently of the other droplets, so that the calculations for the various droplets can be performed successively instead of simultaneously.

This assumption corresponds to the neglect of the nonlinear terms in the differential equation for condensation, which terms are due to consolidation or fission of droplets and depletion or heating of the vapor due to condensation. For the early period of condensation, when the fraction of vapor condensed is still small, these assumptions appear quite accurate, as discussed in greater detail in section 2.1. Therefore, the vapor molecules will be assumed to have velocities and energies distributed according to the Maxwell-Boltzmann relations for the temperature T(t).

The velocities of the droplets ($n > 1$) will also be assumed to correspond to a Maxwellian distribution for the same temperature, T(t). This assumption is justified by the arguments presented in Appendix 2. The rate, $\mathcal{R}_{\text{capt}}$, at which an individual droplet of size n captures vapor molecules is given by Eq. (4) with $i = 1$, $j = n$, and $N_j = 1$:

$$\mathcal{R}_{capt} = K T^{1/2} \beta_{1,n} N_1 . \tag{136}$$

The rate, $\mathcal{R}_{\text{loss}}$, at which a droplet loses molecules is similarly given by Eq. (6) with T replaced by T_n, the temperature of the droplet, and with the free energy difference evaluated at the temperature T_n:

$$\mathcal{R}_{loss} = K T_n^{1/2} \beta_{1,n-1} \exp\left[\frac{(F_n^\circ - F_{n-1}^\circ - F_1^\circ)_{T_n}}{k T_n}\right] . \tag{137}$$

Since Eqs. (136) and (137) give specific transformation rates independent of the time, the time periods during which individual droplets remain unchanged in size follow the familiar exponential decay law, and the probability that the next change in a droplet will occur after a time t is

$$\mathcal{P}_{transf}(t)\,dt = \left(\mathcal{R}_{capt} + \mathcal{R}_{loss}\right) \exp\left[-\left(\mathcal{R}_{capt} + \mathcal{R}_{loss}\right)t\right]dt. \qquad (138)$$

When a given droplet is under consideration, Eq. (138) permits the determination of the time until its next transformation by an appropriate sampling process. A fraction $\mathcal{R}_{capt}/(\mathcal{R}_{capt} + \mathcal{R}_{loss})$ of these transformations will be capture processes; the remainder will be losses.

From kinetic theory,[28] the probability that a given capture process results in the addition to the droplet of a vapor molecule with internal energy E, and relative kinetic energy η is

$$\mathcal{P}_{capt}(E_1,\eta)\,dE_1\,d\eta = \text{const.} \times (E_1)^{\frac{7-5\gamma}{2(\gamma-1)}}\eta$$

$$\times \exp\left[-\frac{E_1+\eta}{kT}\right]dE_1\,d\eta, \qquad (139)$$

where γ is the ratio of the specific heats of the vapor. The constant in Eq. (139) could be evaluated by normalization, but this is not necessary for the application of the Monte Carlo process. The significant parameter, as far as the droplet is concerned, is the total energy, $\Delta E = E_1 + \eta$, contributed by the captured molecule. It is desirable, therefore, to integrate Eq. (139) from $\eta = 0$ to $\eta = \infty$, holding ΔE fixed. This integration yields the probability that the capture of a vapor molecule will increase the droplet energy by ΔE:

$$\mathcal{P}_{capt}(\Delta E)\,d(\Delta E) = \text{const.} \times (\Delta E)^{\frac{3-\gamma}{2(\gamma-1)}} \exp\left(-\frac{\Delta E}{kT}\right) d(\Delta E). \qquad (140)$$

A similar equation for the loss of energy when molecules escape can be readily obtained by considering a droplet at the same temperature as the vapor. By the principle of detailed balance, the evaporating molecules must have the same energy distribution as those condensing. Hence

$$\mathcal{P}_{loss}(-\Delta E)\,d(\Delta E) = const \times (-\Delta E)^{\frac{3-\gamma}{2(\gamma-1)}} \exp\left(\frac{\Delta E}{kT_n}\right) d(\Delta E). \qquad (141)$$

By means of Eqs. (140) and (141), the energy gain or loss for a capture or evaporation process can be properly selected.

To complete the basic equations, relations between droplet temperatures, internal energies and free energies are needed. The droplet free energies are given in terms of their temperatures by Eq. (55), where the constants A and B can be evaluated in various ways, as discussed in section 2.8. The internal energies of n-molecule droplets at a temperature T_n can be obtained from the energy of the vapor, $nkT_n/(\gamma - 1)$, at the same temperature, less the latent energy of vaporization of the bulk liquid, plus the surface energy of the droplet, so that

$$\begin{aligned} E_n(T_n) &= \frac{1}{\gamma-1} n k T_n - n\left[\ell(T_n) + k(T_n)\right] + 4\pi r_n^2 w(T_n) \\ &= \frac{\gamma}{\gamma-1} n k T_n - n\,\ell(T_n) + \left(\frac{6m\sqrt{\pi}}{\rho_L}\right)^{2/3} n^{2/3} w(T_n). \qquad (142) \end{aligned}$$

In Eq. (142), $\ell(T_n)$ is the ordinary latent heat (or enthalpy) of vaporization per molecule; the term kT_n is subtracted from this quantity to give the latent energy of vaporization. The quantity $w(T_n)$ is the surface energy of the liquid per unit surface area. It may be found in tabulated form for some liquids; for others, it can be can be calculated from the surface tension by the relation[12]

$$\omega' = \sigma - T\frac{\partial \sigma}{\partial T}. \tag{143}$$

In these equations, no attempt has been made to introduce a correction for the surface energy of very small droplets similar to Tolman's correction[16] for the surface tension. Derivation of such a correction would require a detailed analysis, but the condensation results probably would be affected only slightly since the surface-energy term in Eq. (142) is generally small compared to the latent heat term.

Equations (138), (140), (141) and (142) comprise the complete set of physical equations necessary for the application of the Monte Carlo method. The purely mathematical details of such a process will not be described here.

TABLE 1

Relative Magnitude of Nonlinear Terms

Condensation of water vapor at 0° C and a
saturation ratio s = 4. (Critical n = 90)

n	Ratio of Nonlinear Terms to Largest Linear Term at t = 0	 at $t \to \infty$ (steady state)
2	-.0005	-1.42
3	-.0007	-1.11
4	.76	- .066
5	.44	- .17
6	.58	- .003
7	.32	- .061
8	.31	- .060
10	.20	- .043
15	.10	- .056
25	.052	- .042
120	---	- .020

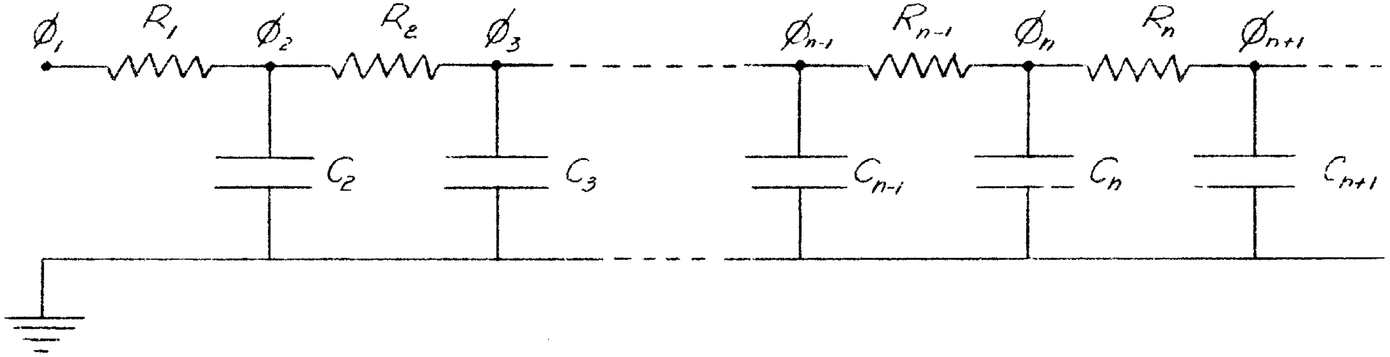


Fig. 1 - Equivalent Network for the Electrical Analogy

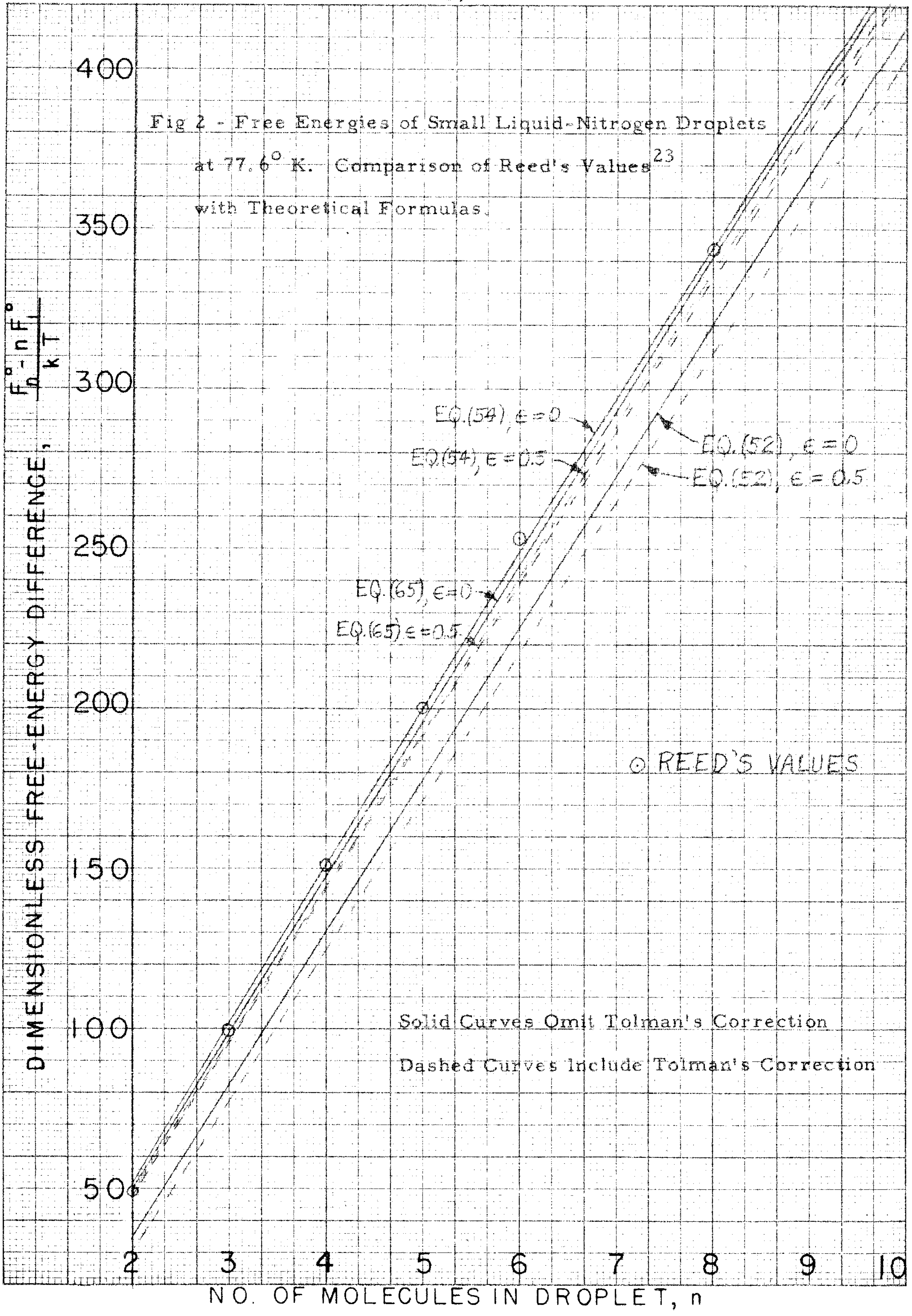


Fig 2 - Free Energies of Small Liquid-Nitrogen Droplets at 77.6° K. Comparison of Reed's Values[23] with Theoretical Formulas.

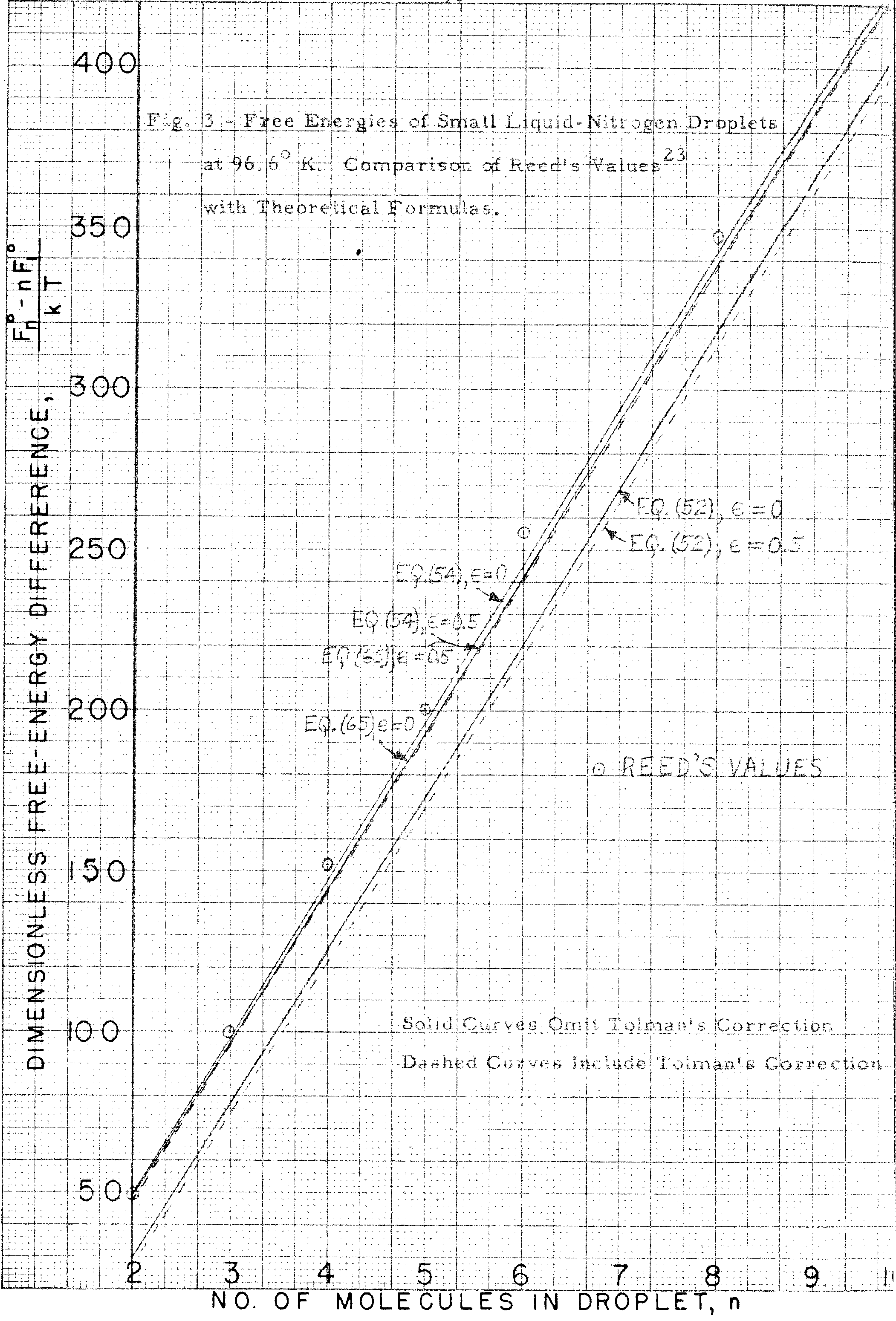


Fig. 3 - Free Energies of Small Liquid-Nitrogen Droplets at 96.6° K. Comparison of Reed's Values[23] with Theoretical Formulas.

Solid Curves Omit Tolman's Correction

Dashed Curves Include Tolman's Correction

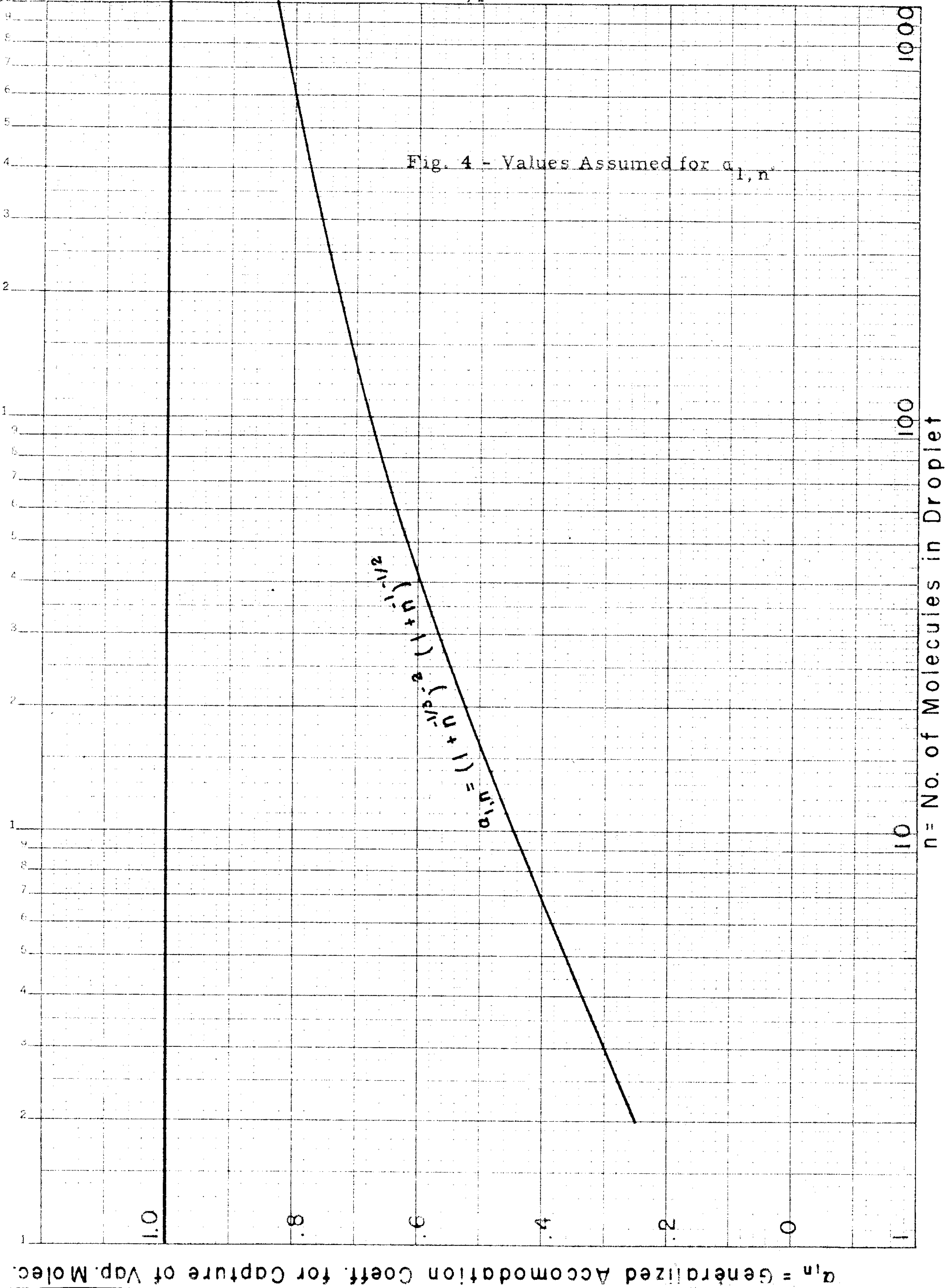


Fig. 4 - Values Assumed for $\alpha_{1,n}$.

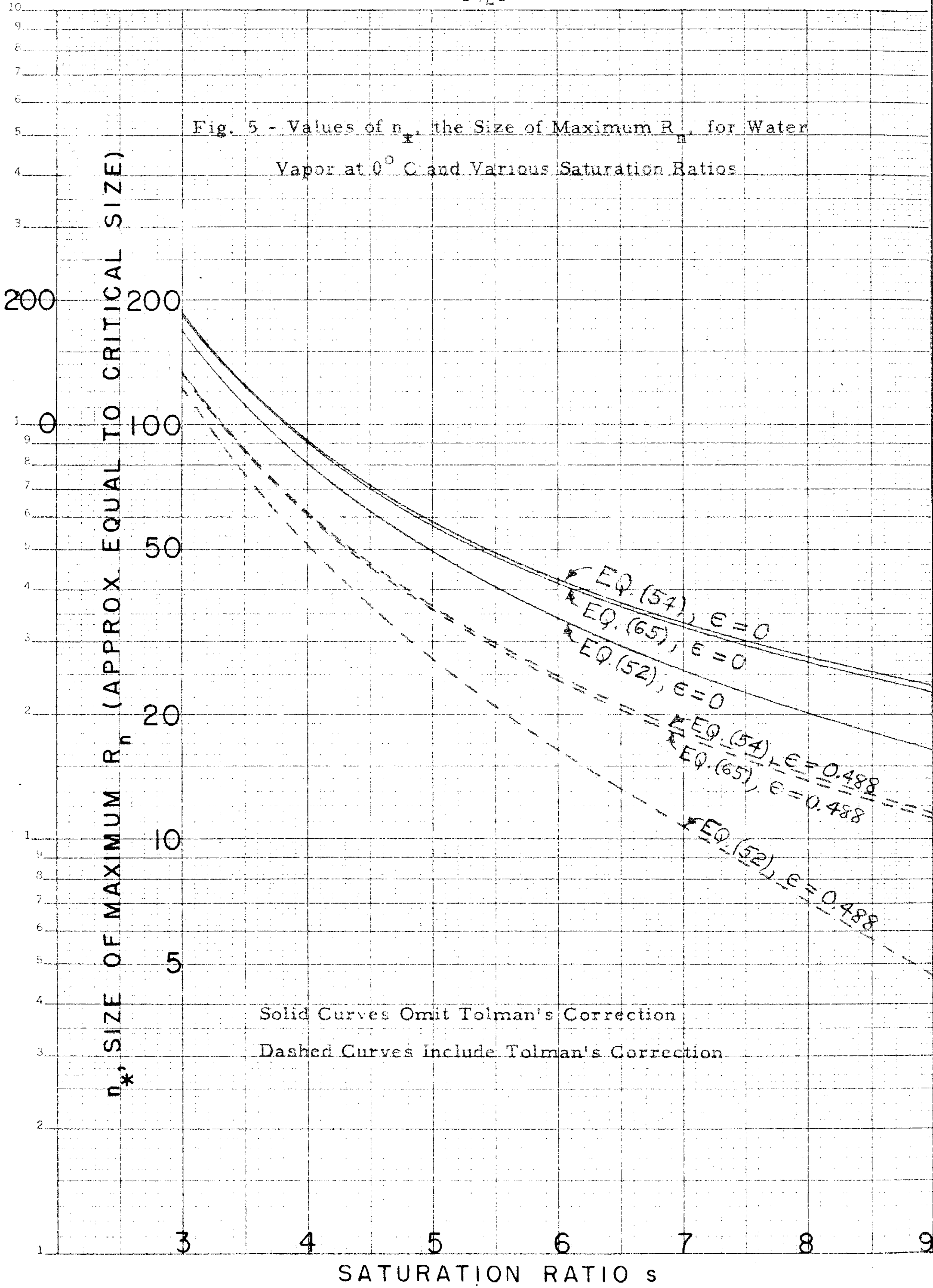


Fig. 5 - Values of n_*, the Size of Maximum R_n, for Water Vapor at 0° C and Various Saturation Ratios

Solid Curves Omit Tolman's Correction

Dashed Curves Include Tolman's Correction

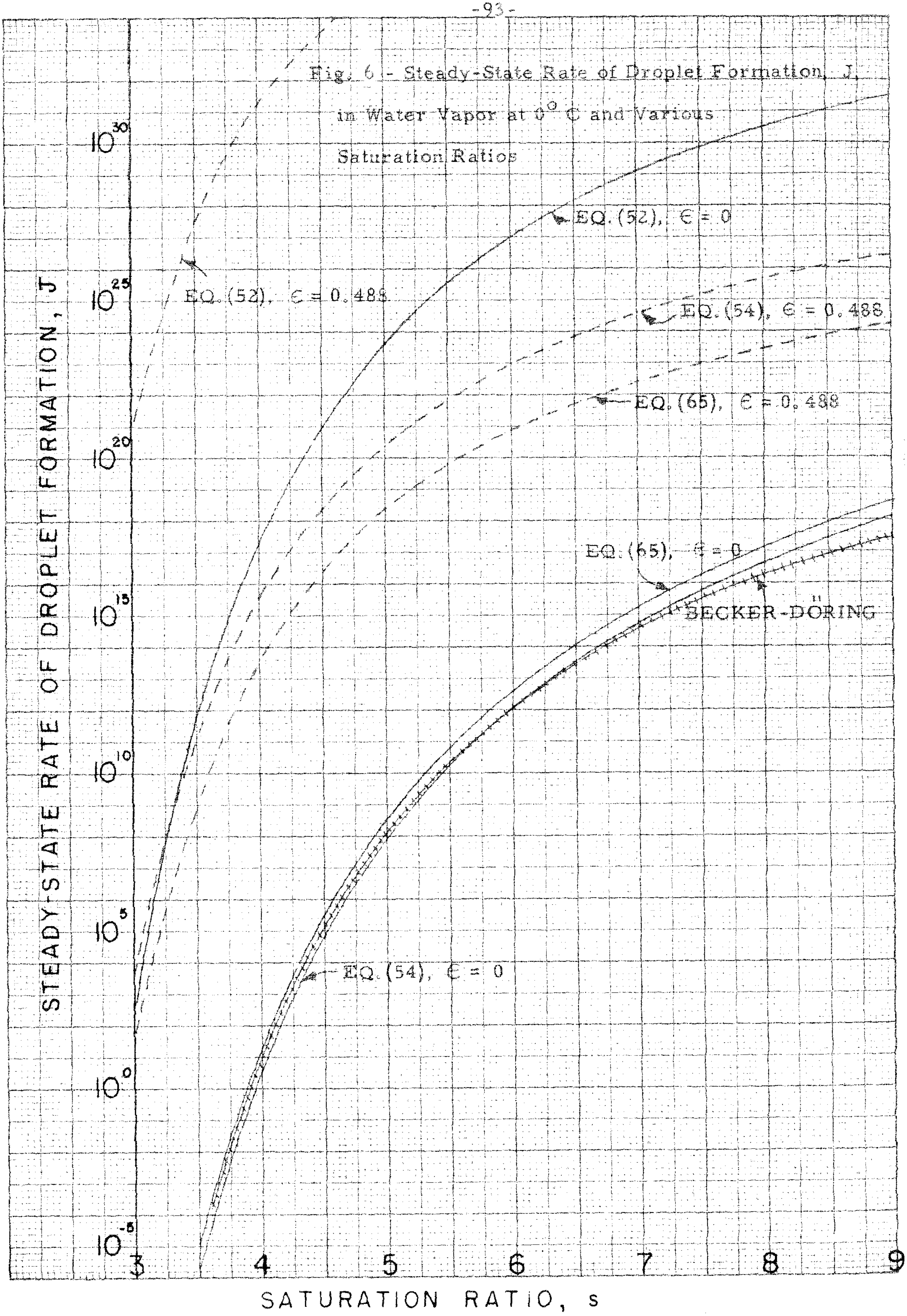


Fig. 6 - Steady-State Rate of Droplet Formation, J, in Water Vapor at 0° C and Various Saturation Ratios

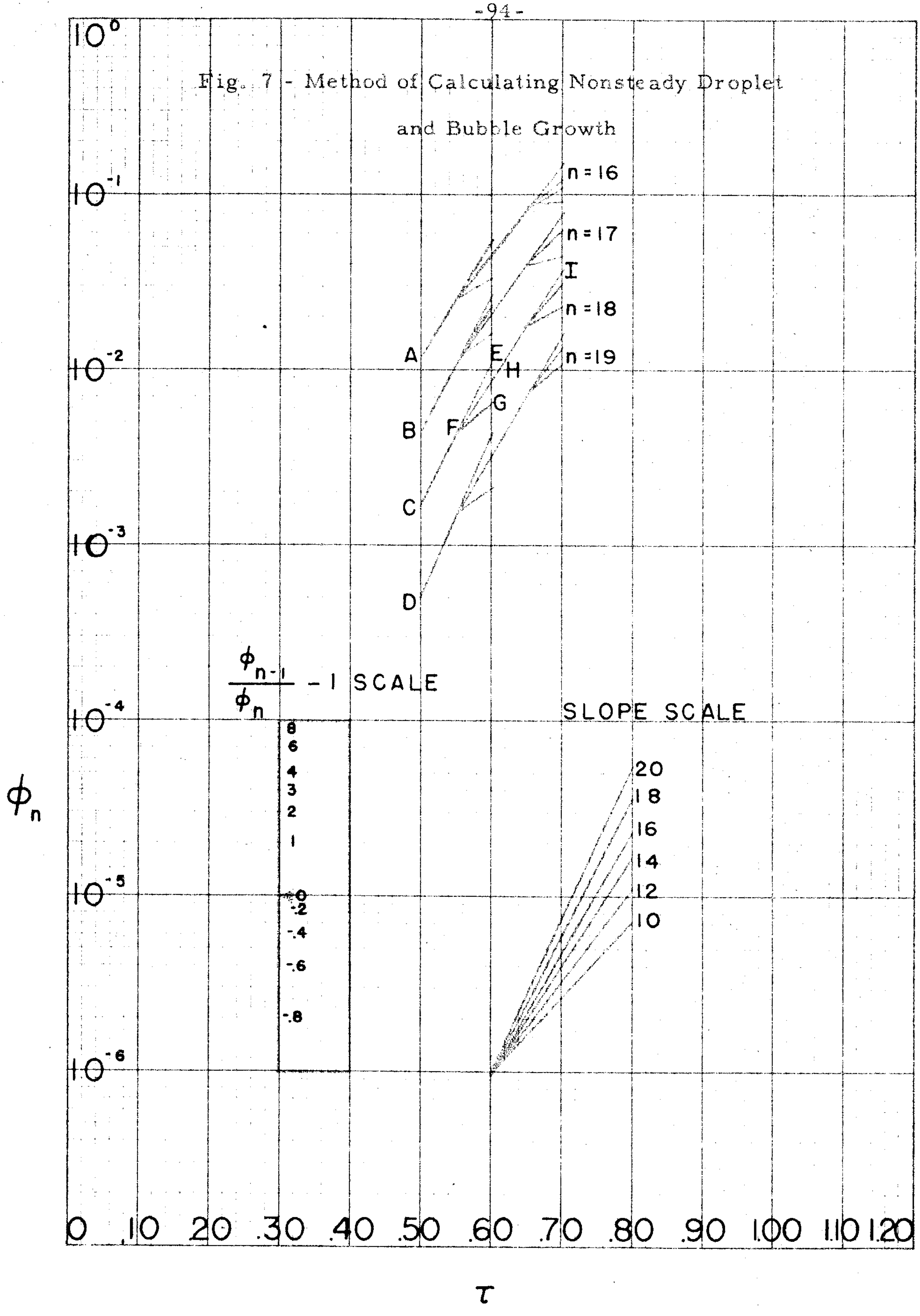


Fig. 7 - Method of Calculating Nonsteady Droplet and Bubble Growth

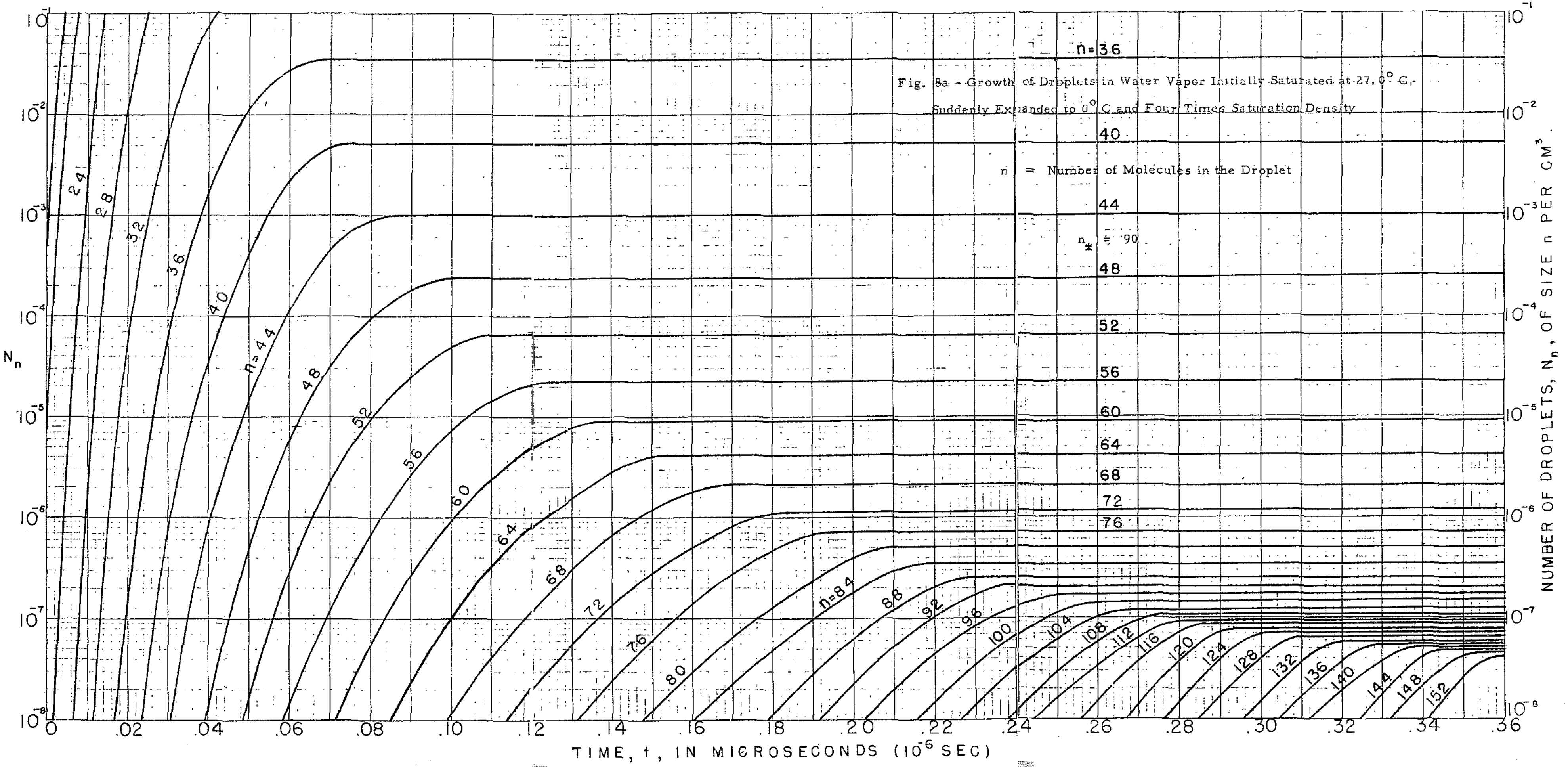


Fig. 8a - Growth of Droplets in Water Vapor Initially Saturated at 27.0° C, Suddenly Expanded to 0° C and Four Times Saturation Density

n = Number of Molecules in the Droplet

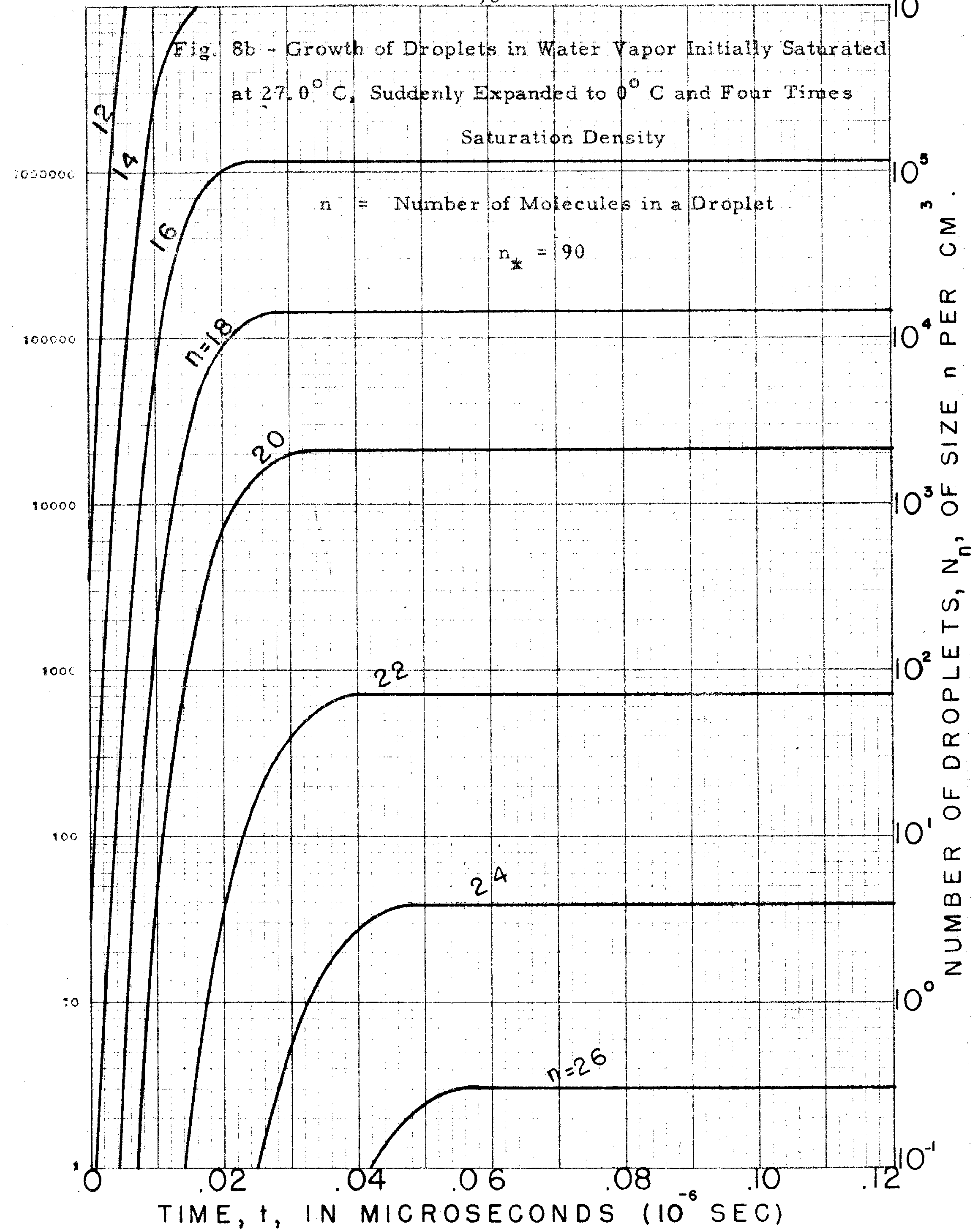


Fig. 8b - Growth of Droplets in Water Vapor Initially Saturated at 27.0° C, Suddenly Expanded to 0° C and Four Times Saturation Density

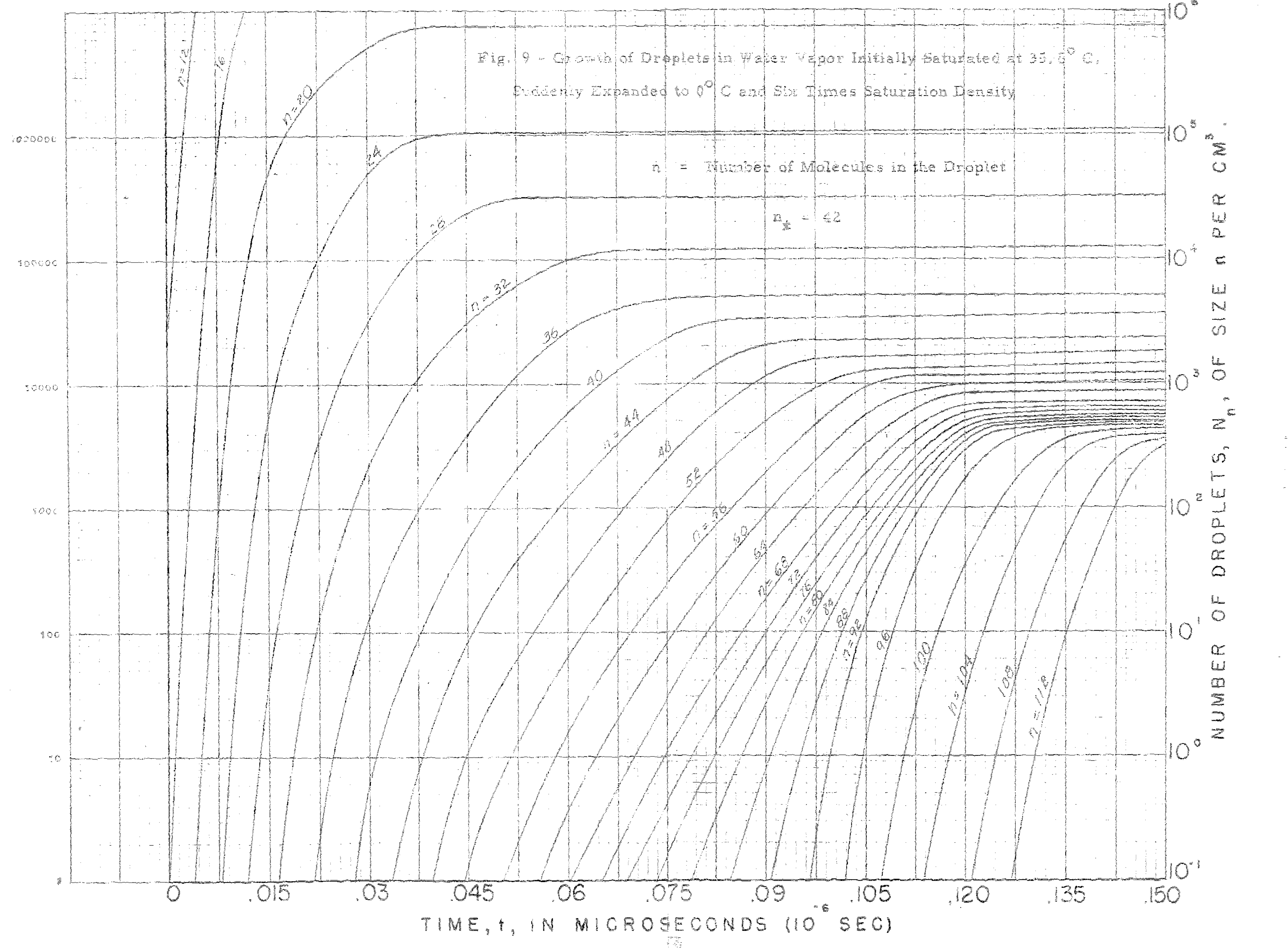


Fig. 9 - Growth of Droplets in Water Vapor Initially Saturated at 35.6° C, Suddenly Expanded to 0° C and Six Times Saturation Density

n = Number of Molecules in the Droplet

$n_* = 42$

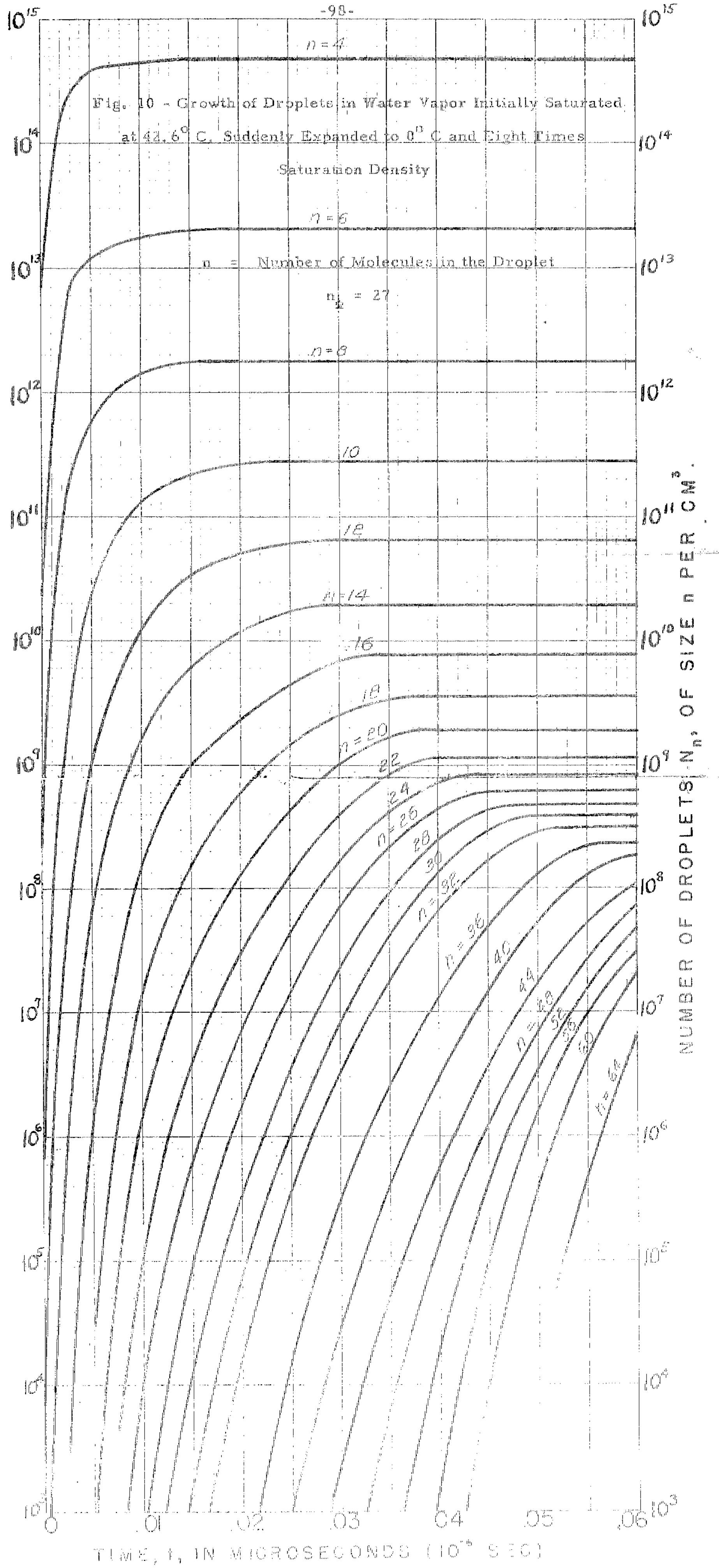
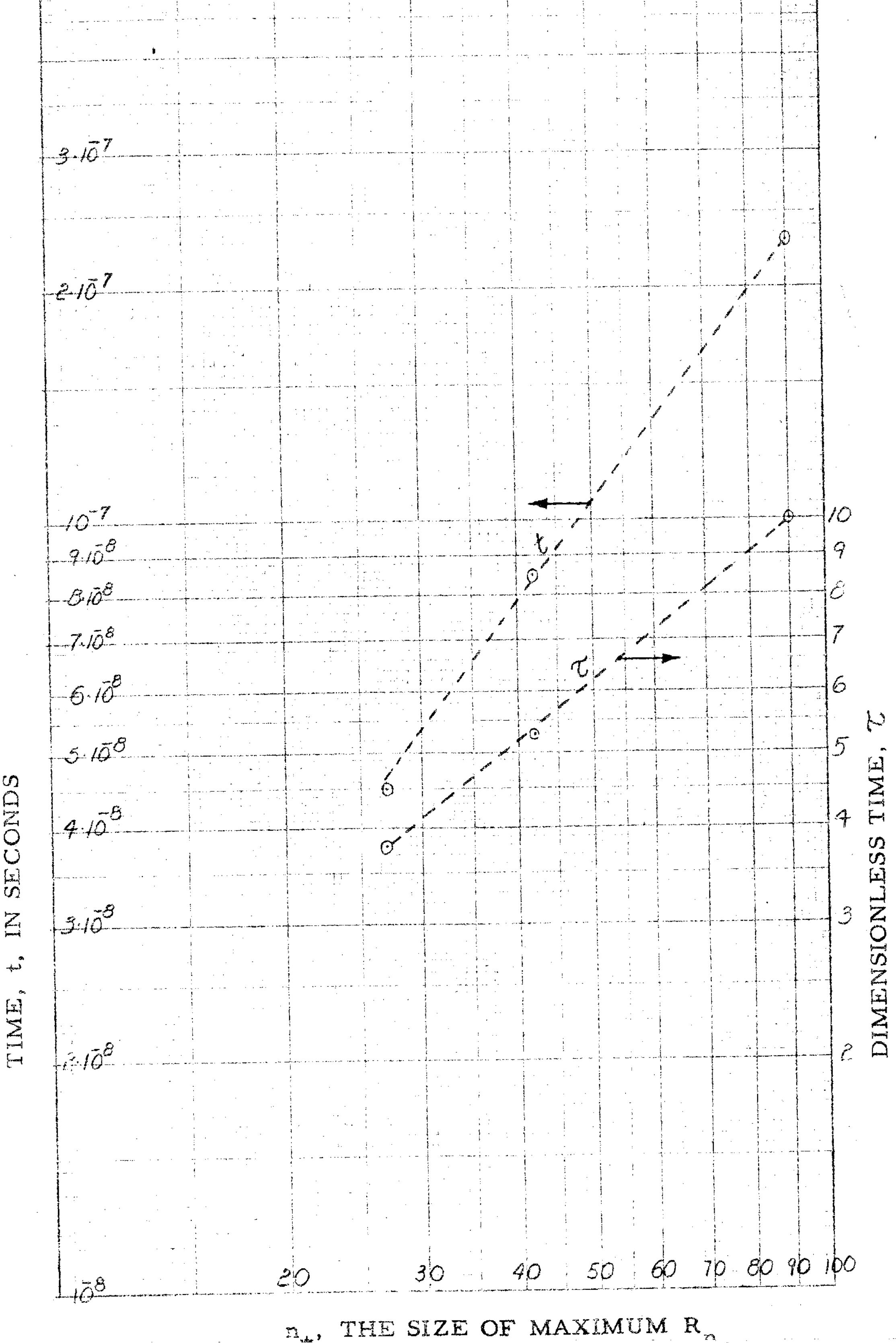


Fig. 10 - Growth of Droplets in Water Vapor Initially Saturated at 42.6° C. Suddenly Expanded to 0° C and Eight Times Saturation Density

n = Number of Molecules in the Droplet

$n_* = 27$

Fig. 11 - Time, t, and Dimensionless Time, τ, for the Number of Droplets of Size n_* (Approx. Critical Size) to Attain the Steady-State Value



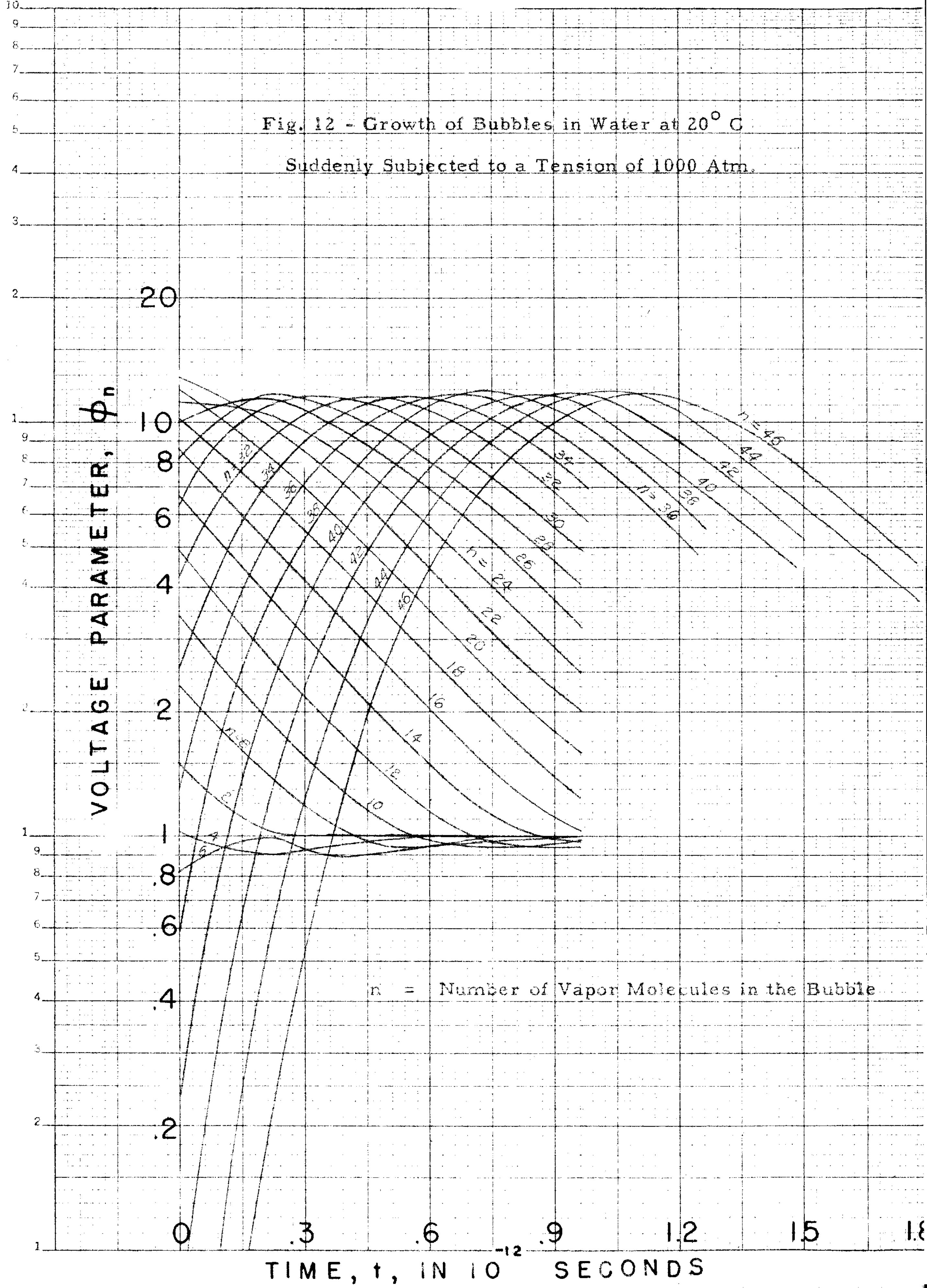


Fig. 12 - Growth of Bubbles in Water at 20° C Suddenly Subjected to a Tension of 1000 Atm.

n = Number of Vapor Molecules in the Bubble