

1963

Vapor condensation under nonequilibrium conditions

Victor Henry Heiskala
Iowa State University

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HEISKALA, Victor Henry, 1938-
VAPOR CONDENSATION UNDER NONEQUILIBRIUM
CONDITIONS.

Iowa State University of Science and Technology
Ph.D., 1963
Engineering, chemical

University Microfilms, Inc., Ann Arbor, Michigan

VAPOR CONDENSATION UNDER NONEQUILIBRIUM CONDITIONS

by

Victor Henry Heiskala

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Nuclear Engineering

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1963

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I. INTRODUCTION

An understanding of the phenomenon of nucleation from a supersaturated metastable phase is essential in the production of colloidal dispersions by condensation methods. In metallurgy, for example, there is the initiation and production of new phases in the formation of alloys; in meteorology, there is fog formation and the artificial production of rain by seeding; in chemical engineering, the unit processes of crystallization, distillation, and evaporation all involve condensation. Also, in recent years, the recognition of the deleterious effects of condensation of a vapor in convergent-divergent rocket nozzles and wind tunnels has led designers to develop apparatus to avoid the region of condensation. Thus, the ability to predict the point in the nozzle at which condensation will occur would be extremely useful to the designer. Finally, besides the academic importance of having fundamental knowledge of the condensation mechanism, the attainment of such knowledge for the design of the high-power-density nuclear plants of the future is essential. These plants will almost certainly require the condensation of a metal vapor as part of their cooling cycle.

The purpose of the present study, then, is to advance a theory which one can extend to situations such as those enumerated. To accomplish this purpose, the plan of approach

is as follows: (1) to assume a plausible mechanism by which condensation can occur, (2) to derive a rate expression, based on this mechanism, for the homogeneous nucleation of the general vapor, (3) to elucidate this general expression for the different types of vapor important in nuclear reactor technology, (4) to account for the effect of surfaces and seeding (heterogeneous nucleation) on the rate of condensation, and (5) to apply the nucleation theory developed to water vapor and compare the results with experimental data.

II. REVIEW OF LITERATURE

The theory of homogeneous nucleation of a condensed phase from a supersaturated phase has been the subject of intensive study for the past forty years. As a consequence, an extraordinary volume of writing has been published concerning this problem. The division of the theory is along three main lines of thought which can be denoted as (1) the liquid drop theory, (2) the constant number theory, and (3) the statistical mechanical theory. General review articles on these divisions are given by Buckle (1), Courtney (2), and Chen-Tsai (3), respectively.

A. Liquid Drop Theory

References (4) through (34) give a chronological review of the literature pertinent to the liquid drop theory of homogeneous nucleation. As seen from the literature, this theory has been applied to liquid-solid transitions (19), nucleation from dilute solutions (20), binary systems (11), and other areas of interest. A short historical development of this theory after Hollomon and Turnbull (22) will be given here.

There are two main assumptions connected with the theory: (1) dense vapor clusters called embryos are formed, grow to the critical size required for nucleation at which point they

are called nuclei, or disappear by a series of molecular collision reactions; (2) the free energy of the dense vapor clusters can be calculated as though they had the same macroscopic surface tension and macroscopic free energy per unit volume as the liquid phase.

Volmer (4) in 1925 based his derivation on the fact that there is a critical size of liquid embryo which can exist in unstable equilibrium with its supersaturated vapor. Through the use of this idea, he was able to calculate the change in free energy which should accompany the formation of such a critical embryo. The number of these critical embryos, or nuclei, is then given according to Volmer as

$$N_g = N \exp \left[\frac{-W}{kT} \right], \quad (1)$$

where N is the number of single vapor molecules, N_g is the number of g -molecule nuclei present, and W is the free energy change associated with the condensation of an individual nucleus. Since embryos smaller than the critical size cannot exist in the metastable vapor phase, he further assumed that the rate of condensation will be proportional to the number of nuclei present at any time. Now, neglecting re-evaporation of the liquid droplets that had formed and assuming that droplets smaller than the critical size will on the average disappear, Volmer found the following result for the volume rate of nucleation

$$R_V = Zg^{2/3} \exp\left[\frac{-W}{kT}\right], \quad (2)$$

where

$$Z = \frac{4\pi p^2}{(2\pi m)^{1/2} (kT)^{3/2}} \left(\frac{3m}{4\pi\rho}\right)^{2/3} \quad (3)$$

and p is the pressure of the vapor, m is the mass per molecule, and ρ is the density of the liquid phase.

In 1935, Becker and Döring (7) improved on Volmer's theory by taking into account the re-evaporation of nuclei into the vapor phase and also by taking into account the decrease in concentration of embryos from the equilibrium concentration because of the depletion due to the rapid growth of the nuclei once they reach the critical size. The effect of this analysis was to introduce the factor $(1/g)^{5/3} (W/3\pi kT)^{1/2}$ into the expression. Their result may thus be written

$$R_{BD} = \frac{Z}{g} \left(\frac{W}{3\pi kT}\right)^{1/2} \exp\left[\frac{-W}{kT}\right]. \quad (4)$$

Zeldovich (8) in 1942 noted that the transient behavior of the growth of embryos closely followed that of the non-stationary diffusion of heat. This line of thought was carried on by Frenkel (9) in 1946, who, by regarding the number of molecules in a near-critical nucleus as constant, i.e., $g - 1 \approx g \approx g + 1$, was able to derive a differential equation for the rate of nucleation based on this assumption.

Hence,

$$R_F = - DN_g \frac{\partial}{\partial g} \left(\frac{f_g}{N_g} \right), \quad (5)$$

where D is a hypothetical diffusion coefficient given by

$$D = 4\pi r^2 N \left(\frac{kT}{2\pi m} \right)^{1/2}, \quad (6)$$

where r is the radius of one of the nuclei and f_g is the time-dependent distribution of g-molecule embryos. Frenkel's solution to (5) can be written

$$R_F = \frac{Z}{g^{1/3}} \left(\frac{W}{3\pi kT} \right)^{1/2} \exp \left[\frac{-W}{kT} \right]. \quad (7)$$

Comparison with the solution of Becker and Döring shows that this latter solution differs only by the factor $g^{-2/3}$. Thus, although the methods used in the theories are quite different, the resulting expressions differ only slightly in the form of the pre-exponential factor. The critical, rate-controlling exponential factor is identical in the three methods.

The greater part of the work beyond this period amounts to improvements in the formulation of the above theories and in the definition of the limits of the applicability of the expressions. For example, because of the suspected decrease in the surface tension for small clusters (17, 22), Courtney (31) takes the lower limit of applicability of the expressions as a 20-molecule cluster. However, Stever (27) and Buckle (1) take the limit as a 10-molecule cluster while Frisch (25)

takes the limit all the way down to a 2-molecule cluster. Be that as it may, it has generally been concluded in the past that experimental data were explained exceptionally well by the liquid drop theory (18, 19, 22, 25, 28). This is surprising in view of the approximations made in formulating the theory and, along these lines, several authors, notably Lothe and Pound (33) and Sundquist and Oriani (34), regard the agreement between the liquid drop theory and experimental data as purely accidental. In fact, recent work by Lothe and Pound (33) indicates that the liquid drop theory may give results a factor of 10^{17} too high.

B. Constant Number Theory

In contrast to the liquid drop theory, the constant number theory assumes that the number of molecules in the critical nucleus is independent of the pressure and temperature of the vapor. This method of nucleation has been proposed by several authors (35-39) and has had some apparent success (24). The volume rate of nucleation can be expressed in this case as (2)

$$R_{CN} = \alpha Z g^{2/3} \exp\left[\frac{-W}{kT}\right], \quad (8)$$

where α , the accommodation coefficient for nucleation, measures the fraction of the vapor molecules which reach temperature equilibrium with the liquid surface before re-evaporating

into the vapor (40). The free energy change involved in the formation of a critical embryo, W , depends in this case on the size assumed for the nuclei of condensation.

C. Statistical Mechanical Theory

A chronological review of the writings in the statistical mechanical field of nucleation is given in references (41) through (49). The time development of this theory of condensation has roughly paralleled that of the liquid drop theory.

The original work in this area was done by van der Waals as reported by Boltzmann in 1898 (41) in which he accounted for the force of attraction between molecules of a gas. However, the first systematic approach to the problem of condensation was made in 1937 when Mayer (42, 43) developed the method of cluster expansion for expressing the virial coefficients (50) of the equation of state in terms of certain integrals involving the intermolecular potential energy. According to this theory, the condensation point is determined by the radii of convergence of the infinite series expressing pressure and specific volume (42). This approach with its subsequent modifications was summarized by Fowler (44) in 1949.

In 1952, Yang and Lee (47, 48) proposed the first truly mathematical model of condensation. They stated that the grand partition function (44) for the vapor can be regarded as a polynomial in the fugacity for a finite volume. Condensation

is then supposed to occur at a certain positive real value of the fugacity toward which the zeros of the fugacity polynomial close in (3). This model has not been overly successful in explaining nucleation.

Although the mathematical rigor employed in the formulation of the statistical mechanical theory may seem to warrant its success, it is generally agreed by proponents of this theory (51) that there does not yet exist a real theory of condensation.

D. Other Theories

One recent theory of condensation, that of Cahn and Hilliard (52), utilizes characteristics common to both the liquid drop and statistical mechanical theories. Whereas the classical liquid drop theory assumes a "sharp interface" model of nucleation in which the liquid and vapor phases are thought to be separated by a distinct interface, the Cahn-Hilliard model assumes a diffuse interface and can thus be thought of as a "diffuse interface" model of nucleation (53). If the interface is diffuse, the free energy required to create a critical nucleus depends on the gradients in density, composition, etc., that exist due to the finite interface. Hence, the free energy of any localized region containing gradients in its properties is supposed to equal the sum of the free energy of the same gradient-free region plus a term propor-

tional to the square of the gradient in that region (34). One sees then, that although the physical model of the liquid drop theory is retained in this theory, the properties of the drop itself are treated from a statistical-mechanical microscopic, rather than a macroscopic, point of view. To date, the Cahn-Hilliard theory has had only partial success in explaining experimental data (34).

III. THE THEORY

A. Mechanism and Rate of Condensation
for the General Vapor1. Fluctuations in the metastable phase

The following description of the formation of stable clusters in a metastable parent phase is paraphrased from Landau and Lifshitz (54).

If a substance is in a metastable state, it will seek to go over from this state to a stable one. This transition can take place in the following way. Due to fluctuations in a uniform phase, embryos of the other phase will form. But, if the original phase is stable, these embryos of the other phase must be unstable and will eventually disappear again. However, if the main phase is metastable, then, for a sufficient size of the embryos formed by fluctuations, the other phase will be more stable than the initial one. In this case, the nuclei of the other phase do not disappear but continue to grow and become centers of transition from the metastable to the stable phase. For example, the liquid drops in a sub-cooled vapor, if large enough, become nucleation centers for the condensation of the vapor.

For each metastable phase, then, there is a minimum size which the embryos of the other phase must have in order to be

more stable than the initial phase. Such embryos of the other phase, having the requisite minimum size, are called nuclei of growth of this phase. The probability of occurrence of such nuclei of growth is calculated in the following.

2. Probability for occurrence of condensation

Consider a subsystem in a medium at an equilibrium temperature and pressure. The probability that this subsystem is in some state different from that of equilibrium (54) is equal to

$$w = \exp \left[\frac{-W}{kT} \right] , \quad (9)$$

where W is the minimum work necessary to take the subsystem out of equilibrium into the given state, k is Boltzmann's constant, and T is the system temperature. This expression for the probability can be utilized in the problem of condensation. The procedure for calculating W for this case is as follows.

When a cluster of molecules (or atoms) in the vapor condenses to the liquid state, the surface area of the droplet that forms will tend to a minimum and thus the shape of the droplet can be taken as spherical. For example, consider the condensation of a g -molecule vapor cluster to form a spherical liquid droplet of radius r . Let r_0 be the radius of one of the single molecules composing the droplet and let v_0 be the

corresponding molecular volume. The minimum work necessary to effect the condensation of the cluster is then just the free energy change involved in the change of state of the g molecules. Thus, if W_L is the free energy per molecule for the liquid phase and W_V is the free energy per molecule for the vapor phase, then the change in free energy for the system due to the condensation of a g -molecule cluster is

$$W = (W_L - W_V)g + 4\pi r^2 \sigma , \quad (10)$$

where σ is the surface tension of the liquid phase at the system temperature. If the volumes of the g molecules before and after condensation are equated

$$v_0 g = \frac{4}{3} \pi r^3 . \quad (11)$$

or,

$$r = g^{1/3} r_0 . \quad (12)$$

Thus, Eq. 10 becomes

$$W = (W_L - W_V)g + 4\pi \sigma g^{2/3} r_0^2 . \quad (13)$$

Now the free energy of the droplet increases with the addition of more particles to the condensed phase. However, one of the criteria for the stability of a system is that the free energy be at a minimum. Therefore, there must be a maximum of the free energy at some size of the condensed

droplet. The size of the droplet at this point is called the critical size and its radius r is the critical radius corresponding to the prevailing temperature and pressure of the vapor. Beyond this critical size, the free energy decreases with the addition of more molecules and the size of the droplet grows without bound. Since at the critical droplet size there must be a maximum in the free energy, then, at this point, $\frac{\partial W}{\partial g} = 0$, or,

$$\frac{\partial W}{\partial g} = 0 = (W_L - W_V) + \frac{2}{3}(4\pi\sigma r_0^2)g^{-1/3}, \quad (14)$$

and,

$$W_L - W_V = -\frac{2}{3}(4\pi\sigma r_0^2)g^{-1/3}. \quad (15)$$

If this result is substituted into Equation 10, there results

$$W = \frac{4}{3}\pi\sigma g^{2/3}r_0^2 = \frac{4}{3}\pi\sigma r^2, \quad (16)$$

where r is the radius of the critical-sized droplet that has been formed.

The probability of a g -molecule vapor cluster changing into a g -molecule spherical droplet is now given by Eq. 9 as

$$w = \exp\left[-\frac{4\pi\sigma r^2}{3kT}\right]. \quad (17)$$

3. Radius of the critical-sized droplet

If p is the pressure of the vapor, p' is the equilibrium vapor pressure at temperature T over a plane surface of the condensed liquid phase, m is the mass per molecule of liquid phase, and ρ' is the density of the liquid phase, then the critical radius of a condensed droplet in the absence of foreign particles is given as (9, 13)

$$r = \frac{2m\sigma}{\rho'kT \ln (p/p')} , \quad (18)$$

or, if p/p' is renamed (33) the supersaturation ratio S ,

$$r = \frac{2m\sigma}{\rho'kT \ln S} . \quad (19)$$

The probability for the condensation of a g -molecule cluster can thus be written

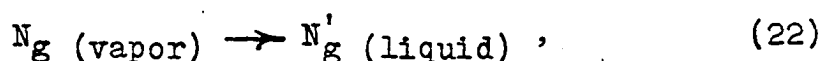
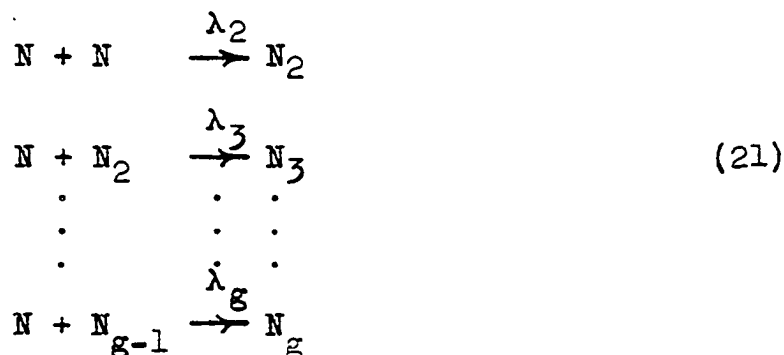
$$\omega = \exp \left[- \frac{16\pi}{3} \left(\frac{m}{\rho' \ln S} \right)^2 \left(\frac{\sigma}{kT} \right)^3 \right] . \quad (20)$$

For convenience, the form of Eq. 17 will be used for the probability in lieu of Eq. 20 in the subsequent development.

4. Cluster mechanism of condensation

In the absence of foreign particles, the only method by which a vapor cluster can occur is through successive vapor molecule collisions. For this reason, the overall reaction

mechanism for the formation of a vapor cluster of g molecules and its condensation to the liquid is assumed to be



where N is the concentration of single vapor molecules, N_j is the concentration of j -molecule clusters, and λ_j is the rate constant for the formation of a j -molecule cluster. Note that the probability for condensation of the critical-sized cluster given by Eq. 20 applies to the step indicated by Eq. 22.

As only the critical-sized droplets are thermodynamically stable in the vapor phase, the contributions to the rate of condensation from embryos less than the critical size should on the average be negligible. Thus, the rate of condensation of the vapor should closely follow the rate of formation of the nuclei of transition. This is equivalent to saying that the rate of condensation will be negligible at a given temperature until the supersaturation ratio becomes such that nuclei of transition can form, at which point the condensation should

occur spontaneously. This has been found to be the case experimentally (13, 15, 22, 29).

The assumption has been made in Eq. 21 that the backward reactions are negligible. This assumption should be valid in nonequilibrium systems in which the driving force in Eq. 21 is definitely to the right. In most practical cases, conditions strongly favor condensation so that this assumption is probably not too greatly in error.

The role of multiple collisions, notably 3-molecule collisions, in the formation of vapor clusters has been neglected in explaining the condensation mechanism. However, this omission appears to be well justified (55).

5. Condensation rate under nonequilibrium steady-state conditions

The nucleation rate under critical temperature and pressure conditions can be expressed as

$$\left[\begin{array}{l} \text{rate of} \\ \text{nucleation} \\ \text{per unit volume} \end{array} \right] = \left[\begin{array}{l} \text{rate of cluster} \\ \text{formation per} \\ \text{unit volume} \end{array} \right] \cdot \left[\begin{array}{l} \text{probability of} \\ \text{cluster condens-} \\ \text{ing to liquid} \end{array} \right] \quad (23)$$

or,

$$R = \frac{dN'_g}{dt} = \frac{dN_g}{dt} \exp \left[\frac{-W}{kT} \right] \quad (24)$$

In order to find dN_g/dt , it is necessary to formulate and solve the differential equations for the concentrations of the

various size embryos. Thus,

$$\begin{aligned}
 \frac{dN_2}{dt} &= \lambda_2 N^2 - \lambda_3 N N_2 \\
 \frac{dN_3}{dt} &= \lambda_3 N N_2 - \lambda_4 N N_3 \\
 &\vdots \\
 &\vdots \\
 \frac{dN_{g-1}}{dt} &= \lambda_{g-1} N N_{g-2} - \lambda_g N N_{g-1} \\
 \frac{dN_g}{dt} &= \lambda_g N N_{g-1} .
 \end{aligned}
 \tag{25}$$

The rate of formation of critical-sized clusters is given by the last of these equations,

$$\frac{dN_g}{dt} = \lambda_g N N_{g-1} .
 \tag{26}$$

In this expression, N_{g-1} is the time-varying concentration of embryos containing $(g - 1)$ molecules, while N is the concentration of single vapor molecules. This latter concentration is assumed to remain constant in time, i.e., the depletion of the vapor due to condensation is assumed to be negligible. Whereas 1 cc. of water vapor at 1 atmosphere and 300°K. contains approximately 2.5×10^{19} molecules and condensation rates less than 10^6 molecules/cc.-sec. can be expected at reasonable supersaturations (21), this assumption appears reasonable.

The solutions to the first two parts of Eq. 25 are

$$N_2 = \frac{\lambda_2 N}{\lambda_3} (1 - e^{-\lambda_3 N t}) \quad (27)$$

$$N_3 = \lambda_2 N \left(\frac{1}{\lambda_4} - \frac{1}{\lambda_4 - \lambda_3} e^{-\lambda_3 N t} \right) (1 - e^{-\lambda_4 N t}) . \quad (28)$$

The succeeding solutions become more and more complex as the critical value is approached; however, their form is the same, i.e., a steady-state solution decreased in value by transient exponential terms whose arguments are of the form $(-\lambda_j N t)$. One sees that the steady-state solutions to Eq. 25 can be written

$$\begin{aligned} N_2^{\neq} &= \frac{\lambda_2}{\lambda_3} N \\ N_3^{\neq} &= \frac{\lambda_2}{\lambda_4} N \\ &\vdots \\ N_{g-1}^{\neq} &= \frac{\lambda_2}{\lambda_g} N . \end{aligned} \quad (29)$$

It can be shown that the difference between these steady-state solutions and their transient counterparts is negligibly small. For example, the difference between N_2^{\neq} and N_2 is given as

$$N_2^{\neq} - N_2 = N_2^{\neq} e^{-\lambda_3 N t} \quad (30)$$

Now, λ_3 is approximately (56, p. 71) equal to 6×10^{-18} at

300°K, since the energy of activation at absolute zero, E_0 , can be set equal to zero (56, p. 249) for these reactions, and N is roughly 2.5×10^{19} , so that $\lambda_3 N \approx 150 \text{ seconds}^{-1}$, and so

$$N_2^{\neq} - N_2 \approx N_2^{\neq} \exp[-150t] . \quad (31)$$

Thus, the transient contribution to the 2-molecule cluster concentration is negligible after a very short time. Also, the magnitude of λ_j is not appreciably different than that of λ_3 so that each of the products $\lambda_j N$ is comparable to $\lambda_3 N$. Thus, after a very short time, one appears justified in using only the steady-state form of the cluster concentrations in the rate expressions.

Making this approximation, the rate of formation of g -molecule clusters per unit volume can be written

$$\frac{dN_g}{dt} = \lambda_g N N_{g-1}^{\neq} = \lambda_2 N^2 , \quad (32)$$

where λ_2 is the rate constant for the first reaction and N is the number of vapor molecules per unit volume. The rate of condensation, according to Eq. 24, is then

$$R = \lambda_2 N^2 \exp\left[\frac{-W}{kT}\right] . \quad (33)$$

6. Reaction rate constants for homogeneous condensation

The reaction rate constant for the j -th reaction, λ_j , can be written (57)

$$\lambda_j = \frac{kT}{h} \frac{\phi_j}{\phi \phi_{j-1}} \exp \left[\frac{-E_0}{RT} \right] ; \quad (34)$$

where h is Planck's constant, R is the gas constant, ϕ_j , ϕ_{j-1} , and ϕ are the partition functions per unit volume for the j -molecule cluster, the $(j - 1)$ -molecule cluster, and for a single molecule of uncollided vapor, and E_0 is the energy of activation for the reaction at the absolute zero of temperature. Although the derivation of the expression for the rate constant is based on equilibrium conditions, the result is valid also under nonequilibrium conditions. (56, 58).

For the case of interest here,

$$\lambda_2 = \frac{kT}{h} \frac{\phi^*}{\phi^2} \exp \left[\frac{-E_0}{RT} \right] , \quad (35)$$

where the sign * refers to the 2-molecule collision complex. The term E_0 is the energy of activation for the 2-molecule reaction at absolute zero and it is taken equal to zero (see preceding discussion). With this substitution, Eq. 35 can be written

$$\lambda_2 = \frac{kT}{h} \frac{\phi^*}{\phi^2} = \frac{kT}{h} F , \quad (36)$$

where the ratio of the partition functions has been replaced

by the symbol F .

Combining Eq. 36 with Eq. 33, the overall rate of condensation can be written

$$R, \frac{\text{nuclei}}{\text{volume-time}} = \frac{kT}{h} FN^2 \exp\left[\frac{-W}{kT}\right], \quad (37)$$

or, in terms of the mass of condensing vapor,

$$R, \frac{\text{mass}}{\text{volume-time}} = \frac{mgkT}{h} FN^2 \exp\left[\frac{-W}{kT}\right], \quad (38)$$

where m is the mass per molecule and g , the number of molecules in a critical-sized cluster, is equal to

$$g = \frac{4\pi r^3 \rho'}{3m}. \quad (39)$$

The expression Eq. 37 applies to the homogeneous nucleation of the general vapor. The factor which is dependent on the particular vapor under consideration is F . It will be shown later that this factor depends on the number of atoms in a single molecule of the vapor, as well as the linearity or nonlinearity of the composite molecule.

In most cases, the vapor can be treated as an ideal gas when finding N , the number of vapor molecules per unit volume. If the vapor cannot be treated as an ideal gas, the following procedure is recommended.

7. Effective pressure for nonideal vapors

In order to account for the deviation of the vapor from an ideal gas, one can use a modification of the perfect gas law, i.e.,

$$pV = CnRT , \quad (40)$$

where the factor C is called the compressibility factor of the gas and it is a function of (1) the type of vapor, (2) the pressure, and (3) the temperature of the vapor. For one mole of vapor, it is defined as

$$C = \frac{pV}{RT} , \quad (41)$$

where p and v are the actual (nonideal) pressure and volume of one mole of vapor at temperature T . The compressibility factor as a function of reduced pressure (actual pressure/critical pressure) and reduced temperature (actual temperature/critical temperature) has been tabulated (57, p. 15).

For a particular temperature and pressure, the number of vapor molecules per unit volume is now given by

$$N = \frac{(p/C)}{kT} . \quad (42)$$

From this point on, the ratio (p/C) will just be denoted by the symbol p . It will be understood that the effective vapor pressure, (p/C) , should be used under nonideal condi-

tions.

If Eq. 42 is substituted for N in Eq. 37, then the condensation rate can finally be written

$$R, \frac{\text{nuclei}}{\text{volume-time}} = \frac{F}{hkT} p^2 \exp \left[\frac{-4\pi\sigma r^2}{3kT} \right]. \quad (43)$$

B. Delineation of the Rate Expression for Specific Vapor Types

The expression Eq. 43 remains general as long as the ratio of the partition functions, F , is left unspecified. When dealing with a particular vapor, however, it is necessary to have an expression for F before the rate of condensation for that vapor can be found. Three separate methods for finding F for common vapors will be given in this section.

There are several types of vapors for which the condensation rate is desired. Among these are the monatomic vapors; this class of vapors includes the metal coolants that are important in high-power-density reactor operation, i.e., sodium, mercury, lead, and others. Another type is the diatomic vapors; this class of vapors includes those gases normally used for reactor coolants such as N_2 or, possibly, H_2 . However, as these gases are not condensed in the cooling cycle used in current technology, they will not be dealt with here (note that alloys such as NaK become individual atoms in the vapor and thus should be treated as a mixture of single

vapor types). A third type of important vapors is hetero-nuclear triatomic and polyatomic molecule vapors; this class includes both linear and nonlinear molecules. Note that most of the organic reactor coolants are either linear or nonlinear polyatomic molecule vapors. A common example of a nonlinear triatomic vapor is ordinary water vapor. A staggered-chain polyatomic organic coolant such as Santowax R ($C_{18}H_{14}$) can probably be approximated as a linear molecule.

1. Statistical mechanical method for finding partition functions

a. Monatomic vapors In the case of a homogeneous monatomic vapor, the activated collision complex will be the diatomic molecule (NN)* which has three degrees of translational freedom and two degrees of rotational freedom. The partition function per unit volume for this complex will thus be given as (59)

$$\phi^* = \left(\frac{4\pi mkT}{h^2}\right)^{3/2} \left(\frac{8\pi^2 IkT}{h^2}\right), \quad (44)$$

where I is the moment of inertia of the activated complex. The activated complex may be pictured as a pair of just-touching spherical balls. If the radius of the nucleus of one of the individual atoms is designated by r_n and the radius of the atom as a whole (including the electron shells) as r_o , the

moment of inertia about a line passing through the center of mass of the pair can be written approximately as

$$I = 2mr_0^2, \quad (45)$$

since $r_0 \gg r_n$ and almost all of the mass is concentrated in the nucleus of the atom. If ξ is used to denote the mean complex diameter, e.g., $\xi = 2r_0$ in this case, then

$$I = \frac{m\xi^2}{2}. \quad (46)$$

The single atoms of the vapor have only three degrees of freedom, all of which are translational. Therefore, the partition function per unit volume in this case will just be the analog to the first factor in Eq. 44, i.e.,

$$\phi = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \quad (47)$$

The ratio of the partition functions for a homogeneous monatomic vapor is thus

$$\begin{aligned} F = \frac{\phi^*}{\phi^2} &= \frac{\left(\frac{4\pi mkT}{h^2} \right)^{3/2} \left(\frac{8\pi^2 kT}{h^2} \right) \left(\frac{m\xi^2}{2} \right)}{\left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right]^2} \\ &= 4h\xi^2 \left(\frac{\pi}{mkT} \right)^{1/2}. \end{aligned} \quad (48)$$

Also, for a mixture of two monatomic vapors A and B, the corresponding expression would be

$$F = \frac{\phi^*}{\phi_A \phi_B} = 2h \xi_{AB}^2 \left[\frac{2\pi}{kT} \left(\frac{m_A + m_B}{m_A m_B} \right) \right]^{1/2}, \quad (49)$$

where m_A , m_B are the respective atom masses.

By substituting Eq. 48 into Eq. 43, one can write for the rate of nucleation of a homogeneous monatomic vapor

$$R = \left(\frac{\pi kT}{m} \right)^{1/2} \left(\frac{2p\xi}{kT} \right)^2 \exp \left[\frac{-4\pi\sigma r^2}{3kT} \right], \quad (50)$$

where ξ is the diameter and m is the mass of an atom of uncol-
lided vapor.

b. Triatomic vapors There are no obvious homonuclear triatomic vapors that would find use as a reactor coolant. Among the heteronuclear triatomic vapors that might find use as a reactor coolant and which might undergo condensation as part of the cooling cycle would be included H_2O , D_2O , NH_3 , CO_2 , and possibly some metal-organic coolants. The heteronuclear triatomic vapors can be further subdivided into those having either nonlinear or linear type molecules. Examples of nonlinear molecules are H_2O , D_2O , and NH_3 . Examples of linear molecules are CO_2 and CS_2 .

The approximation is made here of regarding the partition function for each type of energy as consisting of a number of equal terms, one for each degree of freedom. Thus, if q_T ,

q_R , and q_V denote the contribution to the total partition function, Q , of each translational, rotational, and vibrational degree of freedom, then

$$Q = q_T^t q_R^r q_V^v q_e \quad , \quad (51)$$

where t , r , and v are the numbers of the respective degrees of freedom for each mode. The electronic partition function, q_e , is made to include the nuclear spin contribution. The electronic part of this function can be calculated directly from the observed excited electronic states of the atom or molecule using the relationship (56)

$$q_e = g_n \sum_i g_i \exp \left[\frac{-(\epsilon_i - \epsilon_0)}{kT} \right] \quad . \quad (52)$$

This function will be discussed later in more detail.

A molecule containing n atoms has a total of $3n$ degrees of freedom. A triatomic molecule thus has 9 degrees of freedom to be accounted for.

Note that the atoms within each triatomic (or polyatomic) molecule translate in space as a connected entity. Hence, one may represent the translation of this unit as the translation of the center of mass of its constituent atoms. Since this translation can occur in any of three directions, there are three degrees of freedom, independent of the linearity or non-linearity of the molecule involved, associated with this mode

of energy removal. This leaves $(3n - 3)$ degrees of freedom to be distributed between the internal degrees of freedom for the general polyatomic molecule of n atoms. The distribution of these remaining internal degrees of freedom does depend on the linearity or nonlinearity of the molecule involved.

In order to have a rotational degree of freedom in a certain direction, there must be a moment of inertia associated with that direction. For linear molecules, it is always possible to place one axis along the line of symmetry and, if the masses involved are assumed to be point masses located on this axis (valid for atoms in which all of the mass is concentrated in the nucleus), there is no moment of inertia about this axis. However, there are two moments of inertia associated with the orthogonal axes drawn to this line of symmetry. Hence, for a linear molecule, $q_R^r = q_R^2$. For a nonlinear molecule, there are moments of inertia about each of the orthogonal axes locating the center of mass of the molecule. In this case, $q_R^r = q_R^3$. Thus, for a linear triatomic molecule,

$$Q = q_T^3 q_R^2 q_V^4 q_e, \quad (53)$$

while for a nonlinear triatomic molecule,

$$Q = q_T^3 q_R^3 q_V^3 q_e. \quad (54)$$

Note that the collision between two linear polyatomic molecules will result in a complex which may be either linear

or nonlinear but that the complex formed from the collision of two polyatomic nonlinear molecules must again be nonlinear.

Consider the complex formed by the collision of two linear triatomic molecules. Assume first that the complex is again linear. The partition function for the complex then will be

$$\begin{aligned} Q^* &= q_T^3 q_R^2 q_V^{3(6)-6} q_e^\neq \\ &= q_T^3 q_R^2 q_V^{12} q_e^\neq, \end{aligned} \quad (55)$$

where one degree of vibrational freedom has been removed from the complex and used in evaluating the prefactor $\frac{kT}{h}$ associated with the rate constant (56).

If it is now assumed that the collision complex formed is nonlinear, one may write for its partition function

$$Q^* = q_T^3 q_R^3 q_V^{11} q_e^* , \quad (56)$$

again there being one less degree of vibrational freedom associated with the nonlinear complex molecule. Eq. 56 applies also to the nonlinear complex formed by the collision of two nonlinear triatomic molecules.

Now, the form of q_T has been given as (59)

$$q_T = \left(\frac{2\pi mkT}{h^2} \right)^{1/2} V^{1/3} , \quad (57)$$

and the total rotational partition function for a linear

polyatomic molecule can thus be written (57)

$$q_R^2 = \frac{8\pi^2 I k T}{\beta h^2}, \quad (58)$$

where β is known as the symmetry factor for the molecule. In contrast, the total rotational partition function for a non-linear polyatomic molecule is (57)

$$q_R^3 = \frac{8\pi^2 (8\pi^3 I_1 I_2 I_3)^{1/2} (kT)^{3/2}}{\beta h^3}, \quad (59)$$

where I_1, I_2, I_3 are the principal moments of inertia for the molecule and β , the symmetry factor, is equal to the number of equivalent ways of orientating the molecule in space, e.g., for H_2O , $\beta = 2$; for NH_3 , $\beta = 3$; for CH_4 , $\beta = 12$; for C_6H_6 , $\beta = 12$.

The vibrational partition function is taken over all the different modes of vibration such that

$$q_V^{3n-x} = \prod_i^{3n-x} \left[1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right]^{-1}, \quad (60)$$

where n is the number of atoms in the complex molecule and x depends on the symmetry of the complex molecule, i.e., $x = 6$ for linear molecules, $x = 7$ for nonlinear molecules. The quantity $(3n - x)$ is just the number of degrees of vibrational freedom associated with the molecule. The factor ν_i is the

normal frequency for the i -th mode of vibration of the molecule.

The electronic partition function,

$$q_e = g_n \sum_i g_i \exp \left[\frac{-(\epsilon_i - \epsilon_0)}{kT} \right],$$

can be calculated directly from spectroscopic data for the molecule, if it is known. For a singlet ground state, this factor is different from unity only at high temperatures. The parameter g_i in the expression is the statistical weight associated with the i -th energy state of the atom, i.e., $g_i = 2j_s + 1$, where j_s , which has only positive values given by $l \pm s$, results from the combination of the azimuthal quantum number l and the spin s of the electrons. For example, for a $p_{3/2}$ electronic state, $j_s = \frac{3}{2}$ and $g_i = 2(\frac{3}{2}) + 1 = 4$. The energy decrement, $\epsilon_i - \epsilon_0$, is the difference in energy between the excited level under consideration and the energy of the ground state level. As was mentioned previously, the electronic partition function as defined here includes the nuclear spin contribution, and, since the contribution of the electronic levels may normally be disregarded (59) if their energy is greater than $4kT$, this nuclear spin contribution will usually overshadow the other contributions. One can normally take the electronic partition function as equal to just the nuclear spin contribution.

Rossini (60) finds the total nuclear spin contribution

for the molecule by taking a summation over the nuclear spins for the individual atoms in the molecule. This contribution involves only the sum over the nuclear statistical weights since the ground state energy level for the nucleus is equal to zero (59). For example, neglecting electronic contributions, the partition function for a single water vapor molecule is equal to $q_e = 2 \left[2\left(\frac{1}{2}\right) + 1 \right] + \left[2(0) + 1 \right] = 5$. The corresponding value for the collision complex of two water vapor molecules should be roughly $q_e^* = 4 \left[2\left(\frac{1}{2}\right) + 1 \right] + 2 \left[2(0) + 1 \right] = 10$.

Now, $\phi_1 = Q_1/V$ and $F = \phi^*/\phi^2 = V \cdot Q^*/Q^2$. Therefore, for the collision of two linear triatomic molecules to give a linear complex ($l = \text{linear}$, $nl = \text{nonlinear}$),

$$\begin{aligned}
 F_{l,l} &= \frac{V \cdot (q_T^3 \cdot q_R^2 \cdot q_V^{12} \cdot q_e)^*}{(q_T^3 \cdot q_R^2 \cdot q_V^4 \cdot q_e)^2} \quad (61) \\
 &= \frac{\frac{V \cdot (2\pi m^* kT)^{3/2}}{h^3} \cdot \frac{8\pi^2 I^* kT}{\beta^* h^2} \cdot q_e^* \cdot \prod_i^{12} \left[1 - \exp\left(\frac{-h\nu_i^*}{kT}\right) \right]^{-1}}{\frac{(2\pi m kT)^3 \cdot V^2}{h^6} \cdot \left(\frac{8\pi^2 I kT q_e}{\beta h^2} \right)^2 \left\{ \prod_i^4 \left[1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right]^{-1} \right\}^2} \\
 &= \frac{h^5}{8\pi^2 kT} \cdot \frac{1}{(\pi m kT)^{3/2}} \cdot \frac{\beta^2 I^*}{\beta^* I^2} \cdot \frac{q_e^*}{q_e^2} \cdot \frac{\prod_i^{12} \left[1 - \exp\left(\frac{-h\nu_i^*}{kT}\right) \right]^{-1}}{\left\{ \prod_i^4 \left[1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right]^{-1} \right\}^2}
 \end{aligned}$$

since $m^* = 2m$.

For the collision of two linear molecules to give a

nonlinear complex,

$$\begin{aligned}
 F_{l, nl} &= \frac{V \cdot (q_T^3 \cdot q_R^3 \cdot q_V^{11} \cdot q_e)^*}{(q_T^3 \cdot q_R^2 \cdot q_V^4 \cdot q_e)^2} \quad (62) \\
 &= \frac{\frac{V^2 \cdot (2\pi m^* kT)^{\frac{3}{2}} \cdot 8\pi^2 (8\pi^3 I_1^* I_2^* I_3^*)^{\frac{1}{2}} (kT)^{\frac{3}{2}} q_e^*}{h^3} \cdot \prod_i^{11} \left[1 - \exp\left(\frac{-h\nu_i^*}{kT}\right) \right]^{-1}}{\frac{V^2 \cdot (2\pi m kT)^3 \cdot \left(\frac{8\pi^2 I k T q_e}{\beta h^2}\right)^2 \cdot \left\{ \prod_i^4 \left[1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right]^{-1} \right\}^2}} \\
 &= \frac{1}{(2m)^{3/2}} \cdot \left(\frac{h^2}{\pi kT}\right)^2 \cdot \frac{\beta^2 (I_1^* I_2^* I_3^*)^{1/2}}{\beta^* I^2} \cdot \frac{q_e^* \prod_i^{11} \left[1 - \exp\left(\frac{-h\nu_i^*}{kT}\right) \right]^{-1}}{q_e \left\{ \prod_i^4 \left[1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right]^{-1} \right\}^2}
 \end{aligned}$$

For the collision of two nonlinear molecules to give a nonlinear complex,

$$\begin{aligned}
 F_{nl, nl} &= \frac{V \cdot (q_T^3 \cdot q_R^3 \cdot q_V^{11} \cdot q_e)^*}{(q_T^3 \cdot q_R^3 \cdot q_V^3 \cdot q_e)^2} \quad (63) \\
 &= \frac{\frac{V^2 \cdot (2\pi m^* kT)^{\frac{3}{2}} \cdot 8\pi^2 (8\pi^3 I_1^* I_2^* I_3^*)^{\frac{1}{2}} (kT)^{\frac{3}{2}} q_e^*}{h^3} \cdot \prod_i^{11} \left[1 - \exp\left(\frac{-h\nu_i^*}{kT}\right) \right]^{-1}}{\frac{V^2 \cdot (2\pi m kT)^3 \cdot \left[\frac{8\pi^2 (8\pi^3 I_1 I_2 I_3)^{\frac{1}{2}} (kT)^{\frac{3}{2}} q_e}{\beta h^3} \right]^2 \cdot \left\{ \prod_i^3 \left[1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right]^{-1} \right\}^2}}
 \end{aligned}$$

$$= \frac{1}{\pi^5} \cdot \frac{1}{(8m)^{3/2}} \cdot \left(\frac{h^2}{kT}\right)^3 \cdot \frac{\beta^2 (I_1^* I_2^* I_3^*)^{1/2} q_e^*}{\beta^* (I_1 I_2 I_3) q_e^2} \cdot \frac{\prod_1^{11} \left[1 - \exp\left(\frac{-h\kappa_i^*}{kT}\right) \right]^{-1}}{\left\{ \prod_1^3 \left[1 - \exp\left(\frac{-h\kappa_i}{kT}\right) \right]^{-1} \right\}^2}$$

The rate of nucleation is given by Eq. 43. Substitution of the above expression into this equation gives

$$R_{l,l} = \left(\frac{4\pi n}{m}\right)^{1/2} \cdot \frac{p^2}{m} \cdot \left(\frac{n}{kT}\right)^{7/2} \cdot \frac{\beta^2 I^* q_e^*}{\beta^* I^2 q_e^2} \quad (64)$$

$$\frac{\prod_1^{12} \left[1 - \exp\left(\frac{-h\kappa_i^*}{kT}\right) \right]^{-1}}{\left\{ \prod_1^4 \left[1 - \exp\left(\frac{-h\kappa_i}{kT}\right) \right]^{-1} \right\}^2} \cdot \exp\left[\frac{-4\pi\sigma r^2}{3kT}\right],$$

$$R_{l,nl} = \left(\frac{8\pi^2}{m}\right)^{1/2} \cdot \frac{p^2}{m} \cdot \left(\frac{n}{kT}\right)^3 \cdot \frac{\beta^2 (I_1^* I_2^* I_3^*)^{1/2} q_e^*}{\beta^* I^2 q_e^2} \quad (65)$$

$$\frac{\prod_1^{11} \left[1 - \exp\left(\frac{-h\kappa_i^*}{kT}\right) \right]^{-1}}{\left\{ \prod_1^4 \left[1 - \exp\left(\frac{-h\kappa_i}{kT}\right) \right]^{-1} \right\}^2} \cdot \exp\left[\frac{-4\pi\sigma r^2}{3kT}\right],$$

and,

$$R_{nl, nl} = \left(\frac{2n^2}{m}\right)^{1/2} \cdot \frac{p^2}{m} \cdot \left(\frac{n}{kT}\right)^4 \cdot \frac{s^2(I_1^* I_2^* I_3^*)^{1/2}}{\beta^*(I_1 I_2 I_3)} \cdot \frac{q_e^*}{q_e^2} \quad (66)$$

$$\frac{\prod_i^{11} \left[1 - \exp\left(\frac{-h\nu_i^*}{kT}\right) \right]^{-1}}{\left\{ \prod_i^3 \left[1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right]^{-1} \right\}^2} \exp\left[\frac{-4\pi\sigma r^2}{3kT} \right],$$

where $h = 2\pi\hbar$.

c. Polyatomic vapors The nucleation rate expressions for polyatomic vapors are identical to those for triatomic vapors except that the summation over the vibrational degrees of freedom should be extended. If the polyatomic vapor molecule contains n atoms, the collision complex will contain $2n$ atoms. Therefore, for a linear vapor and a linear complex, the ratio of the product summations over the vibrational degrees of freedom in Eq. 64 should be replaced by

$$(l, l) \rightarrow \frac{\prod_i^{6n-6} \left[1 - \exp\left(\frac{-h\nu_i^*}{kT}\right) \right]^{-1}}{\left\{ \prod_i^{3n-5} \left[1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right]^{-1} \right\}^2} \quad (67)$$

For a linear vapor and a nonlinear complex, the ratio in Eq. 65 should be replaced by

$$(l, nl) \rightarrow \frac{\prod_i^{6n-7} \left[1 - \exp\left(\frac{-h\nu_i^*}{kT}\right) \right]^{-1}}{\left\{ \prod_i^{3n-5} \left[1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right]^{-1} \right\}^2}, \quad (68)$$

while, for a nonlinear vapor and a nonlinear complex, the ratio in Eq. 66 should be replaced by

$$(nl, nl) \rightarrow \frac{\prod_i^{6n-7} \left[1 - \exp\left(\frac{-h\nu_i^*}{kT}\right) \right]^{-1}}{\left\{ \prod_i^{3n-6} \left[1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right]^{-1} \right\}^2}. \quad (69)$$

2. Van der Waals' gas method for finding partition functions

The partition function for a vapor that can be treated as a van der Waals' gas, such as water vapor at moderate temperatures and pressures, has the form¹

$$Q = \frac{(V - nb)^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3/2 N} \exp \left[\frac{-CN^2}{VkT} \right], \quad (70)$$

where n is the number of moles of the gas, b is van der Waals' compressibility constant (61), V is the system volume, and C is a constant yet to be determined.

In order to determine the form of C , it is necessary to relate the partition function to the fugacity of a van der Waals' gas. These parameters are related through the follow-

¹Hansen, Robert S. Partition function for a van der Waals' gas. Ames, Iowa. Private Communication. 1962.

ing series of definitions:

$$a. \quad A = E - TS; \quad A = A(N_1, N_2, \dots, N_i, V, T) \quad (71)$$

$$b. \quad -A/kT = \ln Q \quad (72)$$

$$c. \quad \mu_i = \left(\frac{\partial A}{\partial N_i} \right)_{T, V, N_j} \quad (73)$$

$$d. \quad \frac{\mu_i}{kT} = \frac{\mu_i^0}{kT} + \ln f \quad (74)$$

$$e. \quad \frac{\mu_i^0}{kT} = \lim_{p \rightarrow 0} \left[\frac{\mu_i}{kT} - \ln p \right], \quad (75)$$

where A is the Helmholtz free energy, E is the internal energy, S is the entropy, μ is the chemical potential, f is the fugacity, and p is the pressure of the vapor.

After application of Def. 72 to Eq. 70, one finds

$$\frac{-A}{kT} = N \ln(V - nb) - \ln N! + \frac{3}{2} N \ln\left(\frac{2\pi mkT}{h^2}\right) - \frac{CN^2}{VkT}. \quad (76)$$

But, for large N ,

$$N! = N^N e^{-N} \sqrt{2\pi N}, \quad (77)$$

by Stirling's formula (62). Thus,

$$\ln N! \approx N \ln N - N = N \ln\left(\frac{N}{e}\right) = \ln\left(\frac{N}{e}\right)^N, \quad (78)$$

and Eq. 76 becomes

$$\frac{-A}{kT} = N \ln(V - nb) - \ln\left(\frac{N}{e}\right)^N + \frac{3}{2} N \ln\left(\frac{2\pi mkT}{h^2}\right) - \frac{CN^2}{VkT} \quad (79)$$

Using Def. 73,

$$\begin{aligned} \frac{\mu}{kT} = \frac{\partial}{\partial N} \left(\frac{A}{kT} \right) &= - \frac{3}{2} \ln\left(\frac{2\pi mkT}{h^2}\right) - \ln(kT) + \frac{nb}{V - nb} \\ &+ \frac{2CN}{VkT} - \ln\left(\frac{V - nb}{NkT}\right) . \end{aligned} \quad (80)$$

Since this is also equal to the right side of Def. 74, one can equate the corresponding terms in the two expressions. Hence,

$$\frac{\mu^0}{kT} = - \frac{3}{2} \ln\left(\frac{2\pi mkT}{h^2}\right) - \ln(kT) , \quad (81)$$

and,

$$\ln f = \frac{2CN}{VkT} - \ln\left(\frac{V - nb}{NkT}\right) + \frac{nb}{V - nb} \quad (82)$$

Solving this latter equation for f ,

$$f = \frac{NkT}{V - nb} \exp\left(\frac{2CN}{VkT} + \frac{nb}{V - nb}\right) . \quad (83)$$

The procedure from this point on will be to find a different expression for the fugacity by an independent method and then to equate like parts of the two expressions to find the value of the constant C .

The fugacity of a gas at a given temperature may be defined (57) by the equation

$$d \ln f = \frac{V}{nRT} dp , \quad (84)$$

or, for the change in fugacity between two specified pressures p_A and p_B , as

$$\ln \frac{f_B}{f_A} = \int_{p_A}^{p_B} \frac{V}{nRT} dp . \quad (85)$$

Now, van der Waals' equation can be written (57)

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT , \quad (86)$$

where the constant a accounts for the attraction between molecules of the gas and the constant b accounts for the physical volume that is occupied by the molecules in the gas. The solution for p out of this last equation gives

$$p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} . \quad (87)$$

By changing the variable of integration from p to V in Eq. 85 and letting V_A correspond to p_A , V_B to p_B , one finds after integration,

$$\begin{aligned} \ln \frac{f_B}{f_A} = & - \ln(V_B - nb) + \frac{nb}{V_B - nb} - \frac{2na}{RT} \cdot \frac{1}{V_B} + \ln(V_A - nb) \\ & - \frac{nb}{V_A - nb} + \frac{2na}{RT} \cdot \frac{1}{V_A} . \end{aligned} \quad (88)$$

If $p_A \approx 0$, then $f_A = p_A$ since $\lim_{p \rightarrow 0} \frac{f}{p} \rightarrow 1$ (57, p. 93). Also,

$$\frac{V_A - nb}{V_A} \approx 1, \quad \frac{1}{V_A} \approx 0, \quad \text{and} \quad V_A \approx \frac{nRT}{p_A}.$$

If one uses these approximations in Eq. 88 and takes the antilogarithm of the resulting expression, there results

$$f = \frac{NkT}{V - nb} \exp\left(\frac{nb}{V - nb} - \frac{2Na}{N_0^2 V kT}\right). \quad (89)$$

Equating like parts of Eq. 83 and Eq. 89 shows that

$$C = \frac{-a}{N_0^2}, \quad (90)$$

where a is van der Waals' constant and N_0 is Avogadro's number. Replacing C in Eq. 70 by this last equation, one finds finally for the partition function of a van der Waals' gas

$$Q = \frac{(V - nb)^N}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} \exp\left(\frac{an^2}{V kT}\right), \quad (91)$$

where $n = N/N_0$, is the number of moles of the gas. In the present case, the partition function per molecule is desired. Thus, $N = 1$, $n = (N_0)^{-1}$, and

$$Q = \left(V - \frac{b}{N_0}\right) \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \exp\left(\frac{a}{N_0^2 V kT}\right). \quad (92)$$

Also, for the complex,

$$Q^* = \left(V - \frac{b^*}{N_0} \right) \left(\frac{2\pi m^* kT}{h^2} \right)^{\frac{3}{2}} \exp\left(-\frac{a^*}{N_0^2 V kT} \right) . \quad (93)$$

Substituting these expressions into the rate expression, Eq. 43, and remembering that $F = \phi^*/\phi^2 = VQ^*/Q^2$,

$$R_{VDW} = \frac{Vp^2}{hkT} \frac{\left[\left(V - \frac{b^*}{N_0} \right) \left(\frac{2\pi m^* kT}{h^2} \right)^{\frac{3}{2}} e^{-\frac{a^*}{N_0^2 V kT}} \right]}{\left[\left(V - \frac{b}{N_0} \right)^2 \left(\frac{2\pi m kT}{h^2} \right)^3 e^{-\frac{2a}{N_0^2 V kT}} \right]} \exp\left[-\frac{4\pi\sigma r^2}{3kT} \right] . \quad (94)$$

There are several approximations that can be made in the foregoing equation that simplify its form somewhat. Note, first of all, that $m^* = 2m$, since the collision complex is just a combination of two molecules each of mass m . The van der Waals' constant b^* is related to the volume occupied by the complex molecules and should be roughly equal to twice the corresponding constant for a single molecule in the vapor, i.e., $b^* \approx 2b$. Secondly, the value of the constant a^* should be very near to a since the attraction that is to be considered is much more likely to occur between the complex and an uncollided vapor molecule than between two separate complexes and also since the distance between a complex and an uncollided single molecule should be nearly equal to the distance between two uncollided molecules.

If one employs these approximations in Eq. 94, and notes that $V \approx V - bN_0^{-1} \approx V - b^*N_0^{-1}$, then

$$R_{VDW} = \left(\frac{\pi m}{kT}\right)^{1/2} \left(\frac{2p\hbar}{mkT}\right)^2 \exp\left(\frac{-a}{N_0^2 V kT}\right) \exp\left(\frac{-4\pi\sigma r^2}{3kT}\right), \quad (95)$$

where $\hbar = h/2\pi$. This equation should yield a rough approximation to the nucleation rate for a vapor that can be approximated as a van der Waals' gas.

3. Free energy function method for finding partition functions

This last method for finding the partition function can employ experimental data and thus serves as a check on the other two methods for calculating the partition function.

The partition function for a gas is related to the Gibbs' free energy, G , and the enthalpy, H , by the equation (63)

$$\frac{-(G - H_0)}{RT} = \ln \frac{\phi}{N_0} = \ln \frac{Q}{N_0 V}, \quad (96)$$

where ϕ , the partition function, corresponds exactly to that used in Eq. 51 divided by V , the volume of the system. H_0 is the enthalpy of one mole of the gas at absolute zero and G is the free energy of one mole of the gas at temperature T . Since this free energy function, $-(G - H_0)/T$, is listed as a function of the temperature for different gases and vapors (64, p. 61), the partition function for the uncollided vapor

is relatively easy to find from these data. The partition function for the complex, however, is impossible to find because no experimental values of the free energy function are known for the complex. Two approximate methods for finding the value of the free energy function for the complex state are given in the following.

A review of the values of the free energy functions that are listed for different gases indicates that their range is relatively narrow. Hence, as an approximation, one can assume a value for the free energy function for the complex by likening it to a similar molecule for which the free energy function is known.

A second method of estimating the free energy function for the collision complex involves the summation over the contributions to the function from its separate energy divisions. Hence, one can write for the total free energy function

$$\begin{aligned} \frac{G-H_0}{T} = & \left(\frac{G-H_0}{T} \right)_{\text{translation}} + \left(\frac{G-H_0}{T} \right)_{\text{rotation}} + \left(\frac{G-H_0}{T} \right)_{\text{vibration}} \\ & + \left(\frac{G-H_0}{T} \right)_{\text{electronic}} \end{aligned} \quad (97)$$

The form of the free energy function and other thermodynamic functions has been worked out by Rossini (60). For example, for a monatomic vapor, the free energy function is

$$\frac{G - H_0}{RT} = 1 - \ln \left[v \cdot \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] - \ln q_e . \quad (98)$$

For a linear polyatomic molecule, the corresponding expression is

$$\begin{aligned} \frac{G - H_0}{RT} = 1 - \ln \left[v \cdot \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] - \ln \left(\frac{8\pi^2 I kT}{h^2 \beta} \right) \\ + \sum_i \ln \left[1 - \exp \left(\frac{-h\nu_i}{kT} \right) \right] - \ln q_e , \end{aligned} \quad (99)$$

while, for a nonlinear polyatomic molecule, the appropriate equation is

$$\begin{aligned} \frac{G - H_0}{RT} = 1 - \ln \left[v \cdot \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] - \ln \left[\left(\frac{8\pi^2 kT}{h^2} \right)^{3/2} \frac{(\pi I_1 I_2 I_3)^{1/2}}{\beta} \right] \\ + \sum_i \ln \left[1 - \exp \left(\frac{-h\nu_i}{kT} \right) \right] - \ln q_e . \end{aligned} \quad (100)$$

As an application of this last equation, consider, for example, the collision complex of two water vapor molecules. Assume the complex to consist of the two water molecules connected rigidly between the oxygen atoms and symmetrically arranged about a line drawn through the two atoms. For this assumed arrangement, the free energy function is calculated from Eq. 100 to have the value - 48.2 cal/deg-mole at 300°K, which is

a reasonable value.

The ratio of the partition functions, F , is related to the free energy functions by

$$F = \frac{Q^*/V}{(Q/V)^2} = \frac{1}{N_0} \exp \left[\left(\frac{G - H_0}{RT} \right) - \left(\frac{G - H_0}{RT} \right)^* \right] ; \quad (101)$$

when the functions are expressed on a mole basis. Substitution of the latter equation into Eq. 37 yields the homogeneous nucleation rate of a vapor in terms of the free energy functions for the vapor, i. e.,

$$R_{FE} = \frac{p^2}{hRT} \exp \left[\left(\frac{G - H_0}{RT} \right) - \left(\frac{G - H_0}{RT} \right)^* \right] \exp \left(\frac{-4\pi\sigma r^2}{3kT} \right) . \quad (102)$$

When the expressions, Eq. 98 through Eq. 100, are used to calculate the free energy functions of the complex and single vapor, the resulting rate then becomes equivalent to that based on the earlier statistical mechanical treatment. However, when experimental free energy functions are used in Eq. 102, this treatment becomes independent of the earlier treatment and indeed even provides an experimental check on the previous treatment.

C. Heterogeneous Condensation; Comments on the Theory

Heretofore, only the problem of homogeneous nucleation has been investigated. In this section, the effect of per-

turbations such as surfaces and seeding on the condensation rate will be found. u

1. Surfaces

The method used here to investigate the effect of surfaces will follow that of Landau and Lifshitz (54) for the similar problem of the formation of new layers of a crystal lattice.

Consider the formation of a unimolecular layer of condensed liquid on a surface. Unless the layer is a certain minimum size, it will be unstable and thus return to the metastable vapor. However, once the layer is equal to or greater than the requisite minimum size, it will continue to grow without effort. Let r_0 be the radius of an individual molecule of the layer and R be the radius of the circular unimolecular layer of the required critical size for stability. Since the surface area of the region under consideration will tend to a minimum, the region can be taken as circular. Now, if one can neglect the spaces between the particles on the surface, the number of particles in the layer, N_S , is given by

$$N_S = R^2/r_0^2, \quad (103)$$

from which

$$R = r_0 N_S^{1/2}. \quad (104)$$

The total Gibbs' free energy for the layer is

$$G = N_S \mu , \quad (105)$$

where μ is the chemical potential per particle for the condensed phase. The change in free energy due to the formation of this unimolecular layer would first appear to be just the number of particles in the layer, N_S , times the change in chemical potential per particle that passes from the vapor to the liquid phase. However, in addition to this term, it is necessary to add a term proportional to the surface of separation of the region, i.e., to the perimeter of the region, C . This additional term also includes a factor which depends on the type of surface, its shape and its roughness. The change in free energy for the formation of the region is then

$$\Delta G = N_S(\mu_L - \mu_V) + \tau(\gamma C) , \quad (106)$$

where L, V refer to the liquid and vapor phase, respectively, τ is a constant which depends on surface characteristics, and γ is a linear tension coefficient analogous to the surface tension coefficient.

The circumference of the region can be written

$$C = 2\pi R = 2\pi r_0 N_S^{1/2} , \quad (107)$$

and, thus, ΔG becomes

$$\Delta G = N_S (\mu_L - \mu_V) + 2\pi\tau\gamma r_0 N_S^{1/2} . \quad (108)$$

Whereas the condition for stability of a system is that the free energy be a minimum for that system, the region under consideration will be unstable as long as an increase in the number of particles in the region causes an increase in the free energy of the system. At the point of stability of the region, there must be an inflection point in the free energy change, since, at this point, the free energy must start to decrease upon addition of more particles to the region and, at the point of inflection,

$$\frac{\partial \Delta G}{\partial N_S} = 0 = (\mu_L - \mu_V) + \frac{\pi\tau\gamma r_0}{N_S^{1/2}} , \quad (109)$$

or,

$$N_S = \left(\frac{\pi\tau\gamma r_0}{\mu_V - \mu_L} \right)^2 . \quad (110)$$

This is the minimum number of particles needed to form a stable circular region. Substituting this into Eq. 108 gives the free energy change for the formation of the region,

$$\Delta G = \frac{(\pi\tau\gamma r_0)^2}{\mu_V - \mu_L} . \quad (111)$$

If the condensed region and the surface are at the same temperature, then

$$\mu_V - \mu_L = \delta T (S_V - S_L) , \quad (112)$$

where δT is equal to the temperature of the vapor phase less the temperature of the surface, i.e.,

$$\delta T = T - T_S, \quad (113)$$

and where S_V , S_L are the entropies of the respective phases. If H_L is the latent heat of transition per molecule from the vapor to the liquid phase and if T_W is the transition temperature, then

$$H_L = T_W(S_V - S_L), \quad (114)$$

and thus,

$$\mu_V - \mu_L = H_L \left(\frac{T - T_S}{T_W} \right), \quad (115)$$

so,

$$\Delta G = \frac{(\pi r \gamma r_0)^2 T_W}{H_L (T - T_S)}. \quad (116)$$

The probability of a region forming of the requisite size is given by $\exp[-\Delta G/kT]$. Hence,

$$\omega_R = \exp \left[\frac{-(\pi r \gamma r_0)^2}{k H_L (T - T_S)} \right]. \quad (117)$$

The factor that introduces the effect due to the surface must satisfy three conditions: (1) for a perfectly noninteracting surface and $T = T_S$, the rate should not be affected by the presence of the surface, (2) for a perfectly noninteracting

surface and $T > T_S$, the condensation rate should be greater than the rate for $T = T_S$, and (3) for a perfectly noninteracting surface and $T \gg T_S$, the rate should increase almost without bound. The most general factor that accounts for all the preceding effects is

$$\frac{1}{1 - \omega_R} = \frac{1}{1 - \exp\left[\frac{-(\pi\tau\gamma r_0)^2}{kH_L(T - T_S)}\right]}, \quad (118)$$

with the restriction $T \geq T_S$, i.e., Eq. 118 becomes meaningless if the surface temperature is greater than the vapor temperature.

The general rate expression, including the effect of surfaces, now becomes

$$R = \frac{p_F^2}{hkT} \frac{1}{1 - \exp\left[\frac{-(\pi\tau\gamma r_0)^2}{kH_L(T - T_S)}\right]} \exp\left(\frac{-4\pi\sigma r^2}{3kT}\right). \quad (119)$$

In this expression, the product $(\tau\gamma)$ is unknown analytically and it must be found from experimental data.

2. Seeding

There are two types of seeds which can effect the rate of condensation; these are uncharged particles and charged particles, or ions.

a. Inert particles The effect of introducing an uncharged particle into a body of vapor is just to provide an embryo upon which the vapor can condense. If the seed is less than the corresponding critical size under the given temperature and pressure conditions, the volume of the required nucleus that must form is less by the volume of the seed. If the seed is spherical, its radius is just the radius of the sphere; if the seed is cubical, rectangular, or irregular in shape, it can be approximated as an equivalent volume sphere of radius r_e .

The condensation rate with this correction made becomes

$$R = \frac{p^2 F}{hkT} \frac{1}{1 - \exp \left[\frac{-(\pi r \gamma r_0)^2}{H_L k(T - T_S)} \right]} \exp \left[\frac{-4\pi\sigma(r - r_e)^2}{3kT} \right]. \quad (120)$$

b. Ions There are two effects of introducing a charged particle into the vapor. The first effect is to again physically provide an embryo about which the vapor can condense. The second effect involves the surface energy which results from charging the surface of the spherical droplet. Thus, since the charge originally associated with the ion becomes associated with the droplet which condenses about the ion, the surface energy of the spherical droplet of radius r carrying a charge q_0 in an external medium (taken as air) of

dielectric constant ϵ is given as¹

$$W_{\text{ion}} = \frac{q_0^2}{2\epsilon r} . \quad (121)$$

For small ions, e.g., electrons, the physical size of the ion may be neglected. The physical size of large ions must be accounted for as in Eq. 120.

The predicted rate of condensation about a large ion of radius r_e and charge q_0 should be given by the expression

$$R = \frac{p^2 F}{hkT} \frac{1}{1 - \exp \left[\frac{-(\pi r \gamma r_0)^2}{H_L k (T - T_S)} \right]} \exp \left(\frac{-4\pi\sigma(r-r_e)^2}{3kT} + \frac{q_0^2}{2\epsilon r kT} \right) . \quad (122)$$

3. Summary of assumptions

The following assumptions were made in the derivation of the general rate expression for homogeneous nucleation given by Eq. 43.

- a. The vapors under consideration are all single near-ideal gases.
- b. The mechanism of cluster formation is just the step-wise addition of molecules through collision.
- c. The role of triple and multiple collisions in cluster

¹To charge a spherical capacitor, $W = \frac{1}{2} q_0 V$. But $V = Er$, and $E = 4\pi q_0 / \epsilon A$. Thus, $W = q_0^2 / 2\epsilon r$.

formation is negligible.

- d. The system is not at equilibrium, i.e., the collision reactions are irreversible.
- e. The system is at steady-state as far as the concentration of uncollided vapor is concerned; initial transients can be neglected.
- f. The macroscopic properties of the liquid phase, e.g., surface tension, can be applied to good approximation in the present theory.

4. Qualitative analysis of the rate expression

From the most general rate expression given by Eq. 122, several qualitative conclusions can be drawn in regard to the optimum condensation rate. In general, the condensation rate will be greatest for the following conditions.

- a. The pressure of the vapor is high.
- b. The temperature of the system is moderately high.
- c. The surface tension of the condensed phase is low.
- d. The physical size of seed material is equal to the critical nucleus size for a given temperature and pressure.
- e. The latent heat of vaporization is high.
- f. The surface temperature is low.
- g. The molecular size of the vapor is small.
- h. The charge on any ions present is high.

1. The dielectric constant of the diluent medium is low.

5. Comments on the present study

Although the present development has followed in the main the liquid drop theory of nucleation, there are several areas where this work differs significantly from that of other investigators who have used this model of nucleation.

Perhaps the most important difference is in the form used for the distribution of the critical sized nuclei in the vapor. In this study, partition functions were used to guarantee the correct Boltzmann distribution of nuclei. This method, in itself, is not unique, Frenkel used the same idea in his formulation (9). However, whereas Frenkel employed the partition functions for the g -molecule and $(g - 1)$ -molecule clusters to ascertain his distribution, it has been seen in the present study that, because of the simplifying steady-state approximations that can be made, one need only use the partition functions pertaining to the single vapor molecules and to the 2-molecule clusters to develop the correct Boltzmann distribution. Since the latter functions can be calculated explicitly, the procedure used in this study should give a more correct result.

The delineation of the rate expression for specific vapor types becomes necessary in the present study because of the integral role of the partition functions in the general equa-

tion. This has not been done specifically by other workers either because their assumed distributions did not employ partition functions originally or, as in the case of Frenkel, the partition functions were eliminated en route by assumptions in the course of the development.

The section of this study on heterogeneous nucleation, although original in some aspects, has been primarily an extension of theories arising in other areas to the problem of vapor condensation.

IV. DISCUSSION

In this section the theoretical expressions developed in Section III will be compared with each other and with experimental data when it is possible. Due to the complexity of the calculations and to the lack of data, only the case of the homogeneous nucleation of water vapor will be treated here.

The applicable expressions for the condensation of water vapor by the statistical mechanical, van der Waals, and free energy theories are given by Eq. 66, Eq. 95, and Eq. 102, respectively. Thus,

$$R_{SM} = \left(\frac{2\hbar^2}{m}\right)^{1/2} \cdot \frac{(p'S)^2}{m} \cdot \left(\frac{\hbar}{kT}\right)^4 \cdot \frac{\beta^2 (I_1^* I_2^* I_3^*)^{1/2}}{\beta^* (I_1 I_2 I_3)} \cdot \frac{q_e^*}{q_e^2} \cdot \frac{\prod_i^{11} \left[1 - \exp\left(\frac{-h\kappa_i^*}{kT}\right) \right]^{-1}}{\left\{ \prod_i^3 \left[1 - \exp\left(\frac{-h\kappa_i}{kT}\right) \right]^{-1} \right\}^2} \cdot \exp\left(\frac{-4\pi\sigma r^2}{3kT}\right), \quad (123)$$

$$R_{VDW} = \left(\frac{\pi m}{kT}\right)^{1/2} \left(\frac{2p'S\hbar}{mkT}\right)^2 \exp\left(\frac{-a}{N_0^2 v kT}\right) \exp\left(\frac{-4\pi\sigma r^2}{3kT}\right), \quad (124)$$

and

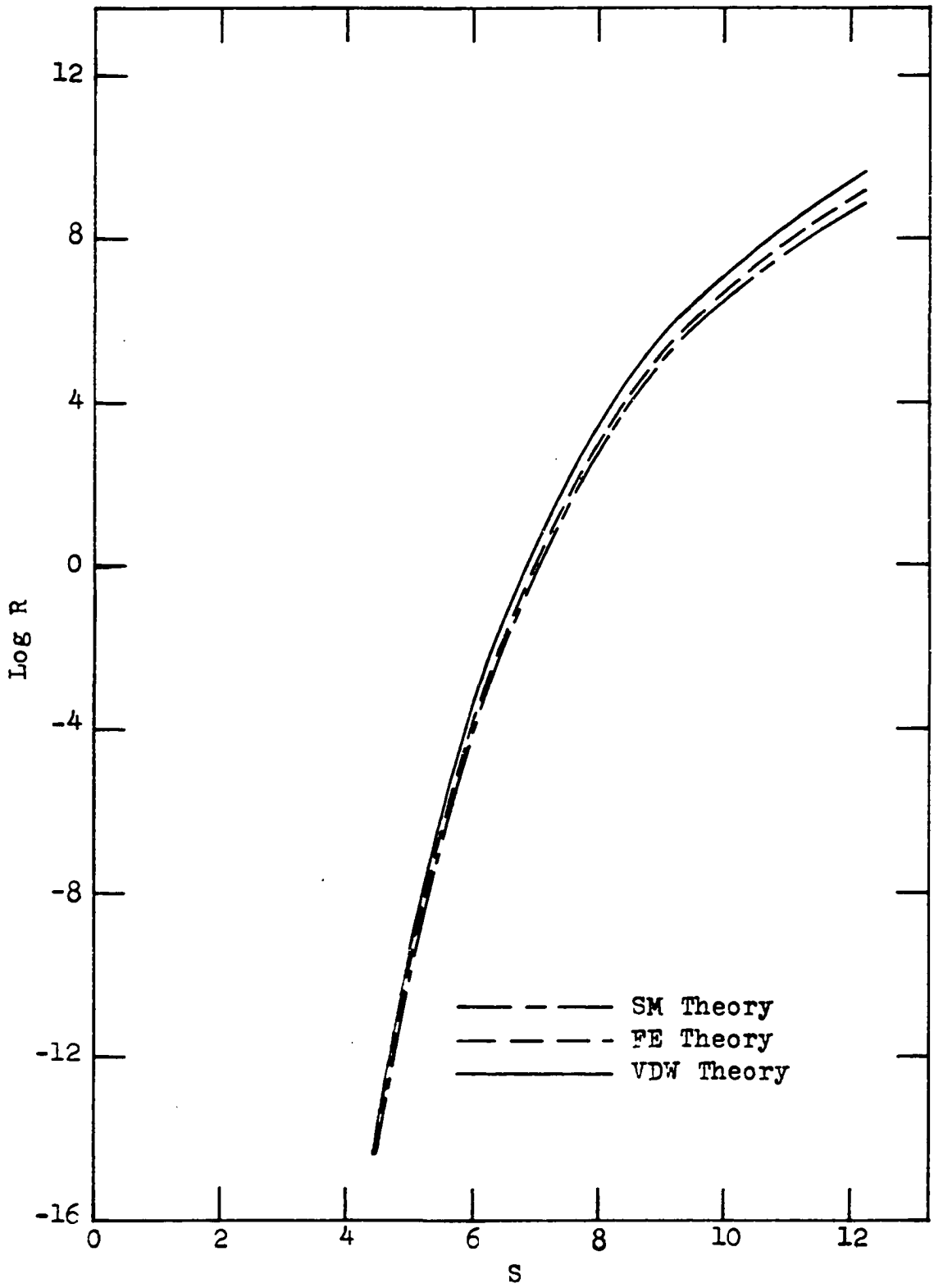
$$R_{FE} = \frac{(p'S)^2}{hRT} \exp\left[\left(\frac{G - H_0}{RT}\right) - \left(\frac{G - H_0}{RT}\right)^*\right] \exp\left(\frac{-4\pi\sigma r^2}{3kT}\right), \quad (125)$$

where the supersaturation ratio, S , is equal to the pressure of the vapor divided by the equilibrium vapor pressure at temperature T over a infinite plane surface of the liquid phase (water, in this case).

The rate of condensation in critical nuclei per cc. per second was calculated from each of these expressions as a function of the supersaturation ratio at a system temperature of 250°K and the results are shown in Figure 1. As seen, the agreement between the theories is excellent at this low temperature. One can probably expect a greater spread in the theories at higher temperatures; in particular, the van der Waals treatment should become less accurate as the vapor starts to deviate significantly from an ideal gas. However, in the range of temperatures for which data are known, i. e., 240°K - 320°K , any one of the three theories can be used for comparison purposes.

It is surprising that, considering the volume of theoretical work that has been done in the area of homogeneous nucleation, there are very few data available with which to compare. The available data can be divided along two lines: those due to Powell (5) and those due to other investigators as summarized by Mason (30). From a review of the literature, this author, along with Lothe and Pound (33), feels that there is only one real set of data for homogeneous nucleation in existence, those of Powell. However, the existing data,

Fig. 1. Condensation rate vs. supersaturation ratio for water vapor at 250°K by different theories



excepting those due to Powell, are summarized in Table 1 for water vapor. The theoretical values of the supersaturation ratio, S , were calculated using Eq. 123 and assuming the nucleation rates suggested in the table.

Table 1. Experimental and calculated supersaturation ratios for the homogeneous nucleation of water vapor

Investigator	T, °K	$R_{\text{obs.}}$	$S_{\text{exp.}}$	$S_{\text{theor.}}$
Wilson (65)	257	$\geq 10^6$	7.90	7.60
Volmer and Flood (6)	261	10^2	5.03	5.85
Frey (66)	263	10^5	5.0	6.30
Sander and Damköhler (67)	261	10^2	4.36	5.85
Barnard (68)	261	10^6	6.60	7.20
Pound, Madonna and Sciulli (30)	261	10^3	5.70	6.15
	238	10^3	6.40	10.35

As seen from Table 1, the agreement between theory and experiment for these data is poor. However, it is re-emphasized that these data are questionable; the known and suspected errors in the data are reviewed by Mason (30).

Powell's data were collected using an all-glass cloud chamber apparatus which kept the ion concentration and other foreign particle influence to a minimum in the experiments. In addition, his data were collected over a wide range of

temperatures and thus provide a more thorough test of the theory. The one objection to the data is the loose definition of the "cloud point" in the condensation. Thus, although the nuclei concentration at the point of condensation is believed to have been about 10^3 nuclei/cc. (30), no original information as to the length of the time of nucleation is available. Based on known duration times of cloud chamber experiments, Barnard (21) has predicted that the rate involved was probably about 10^8 nuclei/cc-second. However, Mason (30), in a similar calculation, predicted a rate of 10^6 nuclei/cc-second.

In the present case, one can estimate this rate by calculating the time necessary to reach steady-state, i.e., the time necessary to make the transient terms in Eq. 27 and Eq. 28 become negligible. As discussed previously, the magnitude of the transient-term exponents is about $\exp(-150 t)$, where t is the time after condensation has started, in seconds. To reduce this term to 0.01, i.e., to drop its value to 1% of the total rate, requires only about 0.03 seconds. The 99% of steady-state rate of nucleation is thus about $10^3/3 \times 10^{-2} \approx 3.3 \times 10^4$ nuclei/cc-second. The range for the value of the rate varies then from about 10^4 to 10^8 nuclei/cc-second. This fact must be kept in mind when making comparisons with the experimental data of Powell, which are summarized in Table 2.

These results are also plotted in Figure 2, where the solid theoretical line corresponds to $R = 10^6$ and the flags

Table 2. Experimental and theoretical supersaturation ratios for the homogeneous nucleation of water vapor at various temperatures

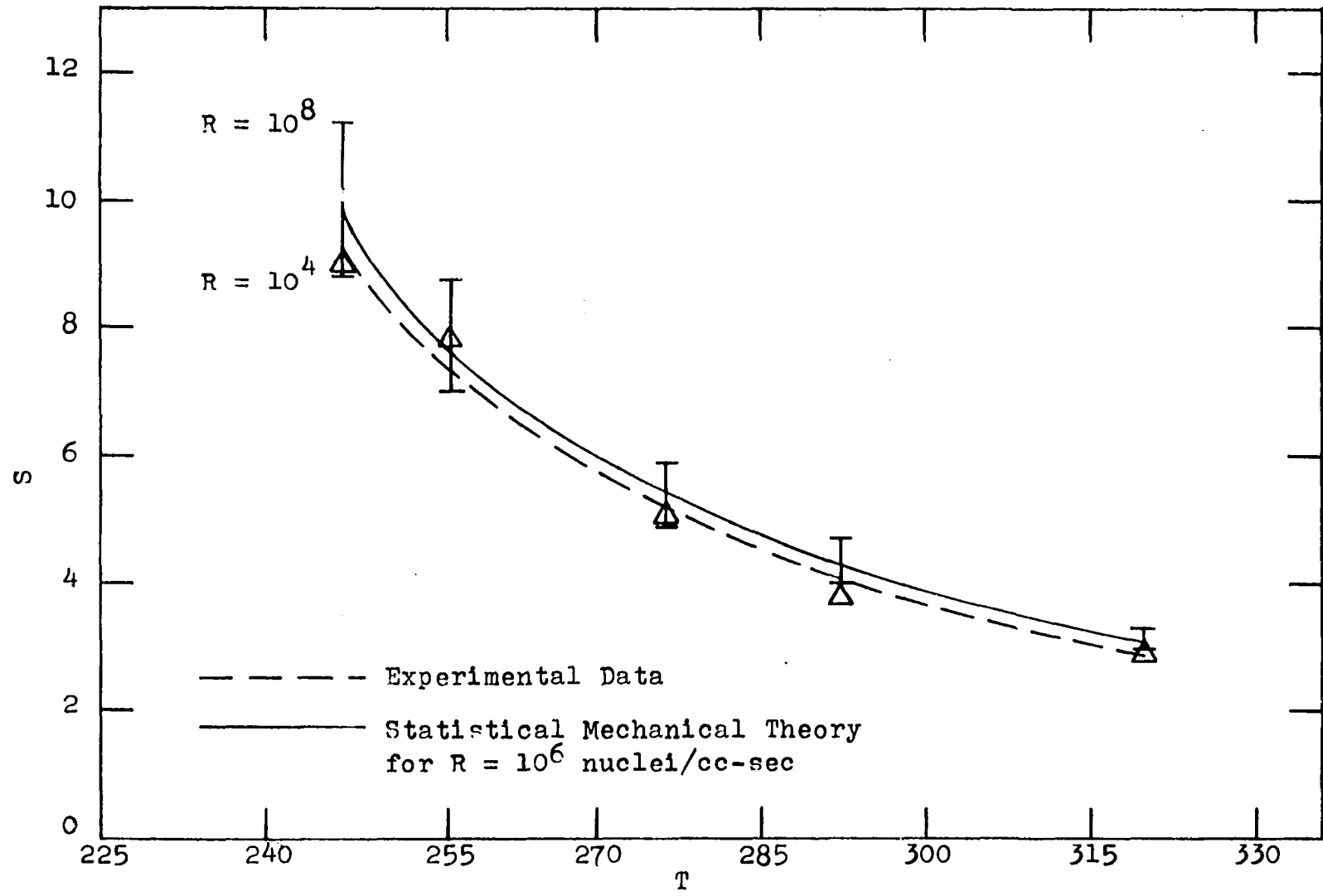
T, °K	S _{exp.}	S _{theor.}		
		R = 10 ⁴	R = 10 ⁶	R = 10 ⁸
246.8	8.95	8.7	9.8	11.2
256.8	7.80	7.0	7.7	8.7
276.4	5.07	4.9	5.4	5.9
292.3	3.74	4.0	4.3	4.7
320.2	2.87	2.9	3.1	3.3

indicate the values of S over the range $R = 10^4$ (lower flag) and $R = 10^8$ (upper flag). One sees from this figure that almost all experimental data are bracketed by the theoretical range of values. In fact, most of the data can be included between the theoretical curves for $R = 10^4$ and $R = 10^6$.

The experimental curve has been drawn by eye to balance deviations in the data rather than using a least-squares fit. The agreement between it and the theoretical curve is good considering the assumptions made in the development of the theory. Note that the effect of an increase or decrease in the rate is just to raise or lower the theoretical curve, that is, the contour will remain virtually the same for these changes.

From the figure, it is seen that, for a nucleation rate

Fig. 2. Experimental and theoretical supersaturation ratios vs. absolute temperature for water vapor



of about 10^5 , there would exist a very close fit between the experimental and theoretical results. This lends weight to the arguments of Mason, who suggests a rate of 10^6 , and also to the present work, which suggests a rate of about 10^4 . However, Barnard's suggested rate of 10^8 seems somewhat too high to explain these data.

V. CONCLUSIONS AND RECOMMENDED
ADDITIONAL STUDIES

A. Conclusions

Based on the good agreement between experimental and theoretical results, the following conclusions regarding the theory of condensation are drawn.

1. The mechanism of cluster formation is the stepwise addition of molecules through collision.
2. Nucleation is a nonequilibrium or irreversible process for which the transient rate of cluster formation can be neglected in comparison to the steady-state rate in less than 0.05 seconds. The steady-state rate of condensation depends directly on the rate of formation of critical sized nuclei in the vapor.
3. Macroscopic data, such as the surface tension, can be applied to good approximation for the nuclei initiating the condensation.
4. At low temperatures and pressures, the partition functions for a vapor can be found by using either the statistical mechanical, the van der Waals, or the free energy function theory developed herein.
5. The effect of seeding on the condensation rate can

be accounted for explicitly; the effect of surfaces on the condensation rate must be explained partially by experimental data.

B. Recommended Additional Studies

As in any lengthy study, many avenues of investigation have been revealed as the work has progressed. Some of the more obvious areas where additional work is required are given.

1. The entire field of homogeneous nucleation is sorely in need of good experimental data; in addition to accumulating more data for water, homogeneous nucleation data for well known organic vapors could also be found with relatively simple equipment.
2. Computer solutions to the expressions developed herein for existing data would help to show more clearly the significance of the present results.
3. The effect of surfaces discussed in this paper should be analysed more thoroughly to determine the form of the product ($\tau\gamma$) which was not determined in the present case.
4. The condensation of pure binary vapor systems, such as NaK in the vapor state, should be investigated; the energy exchange mechanism via collision could probably be treated in a statistical manner.
5. The role of triple and higher-order collisions should

be looked at more closely than it was in this study; in addition, the effect of an inert carrier gas should also be investigated in regard to the mechanism of energy transfer.

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VII. ACKNOWLEDGMENTS

The author wishes to express his deep gratitude to his major professor, Dr. Glenn Murphy, for his guidance, assistance, and encouragement not only during the course of the present study but also in the past. Thanks are also given to Dr. R. S. Hansen, Professor of the Department of Chemistry, for discussions which stimulated portions of this project.

The author expresses his deep appreciation to the United States Atomic Energy Commission for providing fellowship funds without which the study cumulating in this project would have never been possible.

VIII. APPENDIX

A. Note on Vibration Frequencies

The vibration frequencies arising in Eq. 64 through Eq. 66 have been found for different molecules by both spectroscopic and nonspectroscopic methods. An excellent summary of the work in this area is given by Wu (69). His work covers both linear and nonlinear molecules and extends from triatomic to twelve-atomic molecules.

Some idea of the magnitude of the vibrational partition function can be had by calculating this quantity for a water vapor molecule. According to Wu (69, p. 163), the fundamental frequencies of the vibrations are $\kappa_1, \kappa_2, \kappa_3 = 1.103, 0.485, 1.148 \times 10^{14} \text{ sec}^{-1}$. At 300°K, the vibrational partition function is then

$$\prod_{i=1}^3 \left[1 - \exp\left(\frac{-h\kappa_i}{kT}\right) \right]^{-1} \approx \left(1 + \frac{h\kappa_1}{kT}\right) \left(1 + \frac{h\kappa_2}{kT}\right) \left(1 + \frac{h\kappa_3}{kT}\right)$$

$$\approx (1 + 2.04 \times 10^{-8})(1 + 4.2 \times 10^{-4})(1 + 1.04 \times 10^{-8})$$

$$\approx 1. \tag{126}$$

One sees from this calculation that, unless the system temperature is extremely high, the vibrational partition function will always have a value near to unity. Hence, at moderate temperatures, the sum over the vibration states of both

the single vapor and the complex may normally be disregarded.

If it does become necessary to calculate the vibrational partition function for the complex, perhaps the most accurate method is to liken the complex to another molecule for which the vibration frequencies are known. Thus, if it is assumed that the complex formed by the collision of two water vapor molecules has the symmetrical form discussed earlier, one can probably liken the composite structure to that of ethylene, C_2H_4 , where the carbon atoms are quite rigidly bound because of their common double bond. There are eleven vibrational modes associated with the complex; these are shown schematically by Wu (69, p. 262) for the case of C_2H_4 .

Now, with each mode of vibration is associated a frequency of vibration. This frequency is proportional to the energy of the oscillation of the atoms in the molecule and hence is proportional to k , the force constant (spring constant) that exists between atoms in the molecule. For ethylene, the bonds exist between carbon and hydrogen atoms since the carbon-carbon connection lies along the line of decomposition and it is being neglected. The force constant for this type of bonding (69) has the value of 4.9×10^5 dynes/cm. However, for the water vapor collision complex, the appropriate bonding now exists between oxygen and hydrogen atoms for which the force constant has a value (69) of 7.45×10^5 dynes/cm. Thus, one would expect that since $\nu \propto k$, the frequencies

of the normal modes of vibration of the water vapor complex should be different from those of the ethylene molecule by the factor k_{OH}/k_{CH} , or,

$$\kappa^* = \frac{k_{OH}}{k_{CH}} \kappa_{C_2H_4} = 1.52 \kappa_{C_2H_4} . \quad (127)$$

Using Wu's data for ethylene in conjunction with Eq. 127, and noting that

$$\ln \prod_i \left[1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right]^{-1} \approx \sum_i \ln \left[1 + \exp\left(\frac{-h\nu_i}{kT}\right) \right] , \quad (128)$$

one finds for the vibrational partition function for the water vapor complex at 1000°K,

$$\prod_i^{11} \left[1 - \exp\left(\frac{-h\nu_i^*}{kT}\right) \right]^{-1} = 1.982 , \quad (129)$$

while for a single water vapor molecule at 1000°K,

$$\prod_i^3 \left[1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right]^{-1} = 1.107 , \quad (130)$$

so that the ratio of the vibrational partition functions at 1000°K is approximately

$$\frac{\prod_i^{11} \left[1 - \exp\left(\frac{-h\nu_i^*}{kT}\right) \right]^{-1}}{\left\{ \prod_i^3 \left[1 - \exp\left(\frac{-h\nu_i}{kT}\right) \right]^{-1} \right\}^2} \approx 1.6 . \quad (131)$$

A similar analysis would have to be carried out for the collision complexes formed from other vapors. However, in the usual case, the required ratio can be set equal to unity.

B. Note on Moments of Inertia

The mass of an atom is concentrated in its nucleus and hence a molecule may be treated as a system of point masses when finding its moments of inertia.

For a linear molecule containing n atoms which have masses $m_1, m_2, m_3, \dots, m_n$, there will be no moment of inertia about the axis of symmetry of the molecule and the moments about the other orthogonal principal axes will be equal. It can be assumed in all calculations that the centers of mass of two adjacent atoms are separated by a distance equal to the sum of their respective bond radii. If the center of mass of the composite molecule is at a distance \bar{r} from the furthestmost left mass which is taken as m_1 , then,

$$\bar{r} = \frac{\sum_{k=1}^{n-1} m_{1+k} (r_1 + 2 \sum_{j=1}^{k-1} r_{1+j} + r_{1+k})}{\sum_{k=1}^n m_k}, \quad (132)$$

and, if the moments of inertia of the nuclei of the atoms are neglected because of their comparatively small radii, the moment of inertia of the molecule about an axis through the center of mass is just

$$I = m_1 \bar{r}^2 + \sum_{k=1}^{n-1} m_{1+k} (r_1 + 2 \sum_{j=1}^{k-1} r_{1+j} - \bar{r})^2, \quad (133)$$

where r_1 is the atomic radius of the first atom, and so on.

For a nonlinear planar molecule containing n atoms, there are two moments of inertia about perpendicular axes through the center of mass of the molecule and lying in its plane, i.e., $I_{\bar{x}}$ and $I_{\bar{y}}$, and a third moment of inertia, $I_{\bar{z}}$, about an axis passing through the center of mass and perpendicular to the plane of the molecule. Note that due to the plane symmetry, $I_{\bar{z}} = I_{\bar{x}} + I_{\bar{y}}$.

Now, if \bar{x} is the distance measured horizontally from the furthestmost left atom to the center of mass and \bar{y} is the distance measured vertically from the uppermost atom to the center of mass, then,

$$\bar{x} = \frac{\sum_{i=1}^{n-1} m_{1+i} x_{1+i}}{\sum_{i=1}^n m_i}, \quad (134)$$

and,

$$\bar{y} = \frac{\sum_{i=1}^{n-1} m_{1+i} y_{1+i}}{\sum_{i=1}^n m_i}. \quad (135)$$

The corresponding moments of inertia are then

$$I_{\bar{x}} = m_1 \bar{x}^2 + \sum_{i=1}^{n-1} m_{1+i} (x_{1+i} - \bar{x})^2, \quad (136)$$

$$I_{\bar{y}} = m_1 \bar{y}^2 + \sum_{i=1}^{n-1} m_{1+i} (y_{1+i} - \bar{y})^2, \quad (137)$$

and,

$$I_{\bar{z}} = m_1 (\bar{x}^2 + \bar{y}^2) + \sum_{i=1}^{n-1} m_{1+i} [(x_{1+i} - \bar{x})^2 + (y_{1+i} - \bar{y})^2]. \quad (138)$$

For a nonlinear nonplanar polyatomic molecule of n atoms, there are three separate moments of inertia about orthogonal axes drawn through the center of mass. The location of the center of mass is given in terms of the distance from the furthestmost left atom as

$$\bar{x} = \frac{\sum_{i=1}^{n-1} m_{1+i} x_{1+i}}{\sum_{i=1}^n m_i}, \quad (139)$$

$$\bar{y} = \frac{\sum_{i=1}^{n-1} m_{1+i} y_{1+i}}{\sum_{i=1}^n m_i}, \quad (140)$$

and,

$$\bar{z} = \frac{\sum_{i=1}^{n-1} m_{1+i} z_{1+i}}{\sum_{i=1}^n m_i}, \quad (141)$$

where \bar{x} , \bar{y} , \bar{z} are measured from the yz-, xz-, and xy-planes passing through the furthestmost left atom. The corresponding moments of inertia (through the center of mass) are then

$$I_{\bar{x}} = I_{\overline{xy}} + I_{\overline{xz}} \quad (142)$$

$$= m_1(\bar{y}^2 + \bar{z}^2) + \sum_{i=1}^{n-1} m_{1+i} \left[(y_{1+i} - \bar{y})^2 + (z_{1+i} - \bar{z})^2 \right],$$

$$I_{\bar{y}} = I_{\overline{yx}} + I_{\overline{yz}} \quad (143)$$

$$= m_1(\bar{x}^2 + \bar{z}^2) + \sum_{i=1}^{n-1} m_{1+i} \left[(x_{1+i} - \bar{x})^2 + (z_{1+i} - \bar{z})^2 \right],$$

and,

$$I_{\bar{z}} = I_{\overline{zx}} + I_{\overline{zy}} \quad (144)$$

$$= m_1(\bar{x}^2 + \bar{y}^2) + \sum_{i=1}^{n-1} m_{1+i} \left[(x_{1+i} - \bar{x})^2 + (y_{1+i} - \bar{y})^2 \right].$$

It becomes apparent from these formulas that, in order to calculate the moments of inertia for the collision complex, it is necessary to assume a configuration for the complex. One method of doing this is to select the configuration associated with the most probable mode of collision. To be accurate, however, one should treat all possible collision models.

Previously, the collision complex of two water molecules has been assumed to be a symmetrical affair arranged about a rigid connection of the oxygen atoms in the molecules. Using this model and taking the bond angle (57) as 105° for the

water molecule, one can find the moments of inertia by employing the expressions Eq. 136 through Eq. 138. Thus,

$$I_{\bar{x}}^* = 33.45 \times 10^{-40} \text{ g-cm}^2 ,$$

$$I_{\bar{y}}^* = 3.86 \times 10^{-40} \text{ g-cm}^2 ,$$

and,

$$I_{\bar{z}}^* = 37.31 \times 10^{-40} \text{ g-cm}^2 .$$

These values are the same order of magnitude (69, p. 268) as those found experimentally for ethylene, C_2H_4 , which has basically the same model configuration.

C. Note on Electronic Partition Functions

The electronic partition function of an atom, including the nuclear spin contribution, can be written (60) as

$$\begin{aligned} q_e &= g_n \sum_{i=0}^L g_i e^{-(\epsilon_i - \epsilon_0)/kT} \\ &= g_n \left[g_0 + g_1 e^{-(\epsilon_1 - \epsilon_0)/kT} + g_2 e^{-(\epsilon_2 - \epsilon_0)/kT} + \dots \right. \\ &\quad \left. + g_L e^{-(\epsilon_L - \epsilon_0)/kT} \right] , \end{aligned} \tag{145}$$

where L is the total number of energy levels corresponding to the excited electronic states of the atom and g_n is the statistical weight associated with the ground state of the nucleus.

The multiplicity of the ground state energy levels depends on the atom under consideration. For example, for ${}_{17}\text{Cl}^{35}$, the ground state configuration (70) is the inverted ${}^2\text{P}$ doublet, i.e., ${}^2\text{P}_{3/2}$ and ${}^2\text{P}_{1/2}$ for lower and upper levels, respectively. Thus, since the j_s values are $3/2$ and $1/2$, the statistical weights are then $g_{3/2} = 4$ and $g_{1/2} = 2$, respectively. As an example of a singlet ground state, consider the electronic partition function for sodium. The ground state (70) is the singlet ${}^2\text{S}_{1/2}$. Thus, $l = 0$, $s = 1/2$, and $j_s = 1/2$, so $g_{1/2} = 2$. This is the electronic contribution to the partition function since the ground state is singlet and thus $\epsilon_1 - \epsilon_0 = 0$ (neglecting higher electronic states). The nuclear spin of sodium is $3/2$ and the spin contribution g_n is equal to 4. The total electronic partition function is thus $q_e = 4(2) = 8$. For monatomic vapors whose ground state is not singlet, the values of the distinct energy states can be found from the data of Bacher and Goudsmit (71).

The electronic contribution to the partition function for the collision complex of two molecules is usually impossible to find because of the lack of knowledge of energy states for the complex. The same is true for simple molecules. Thus, for comparison purposes in the present development, the total electronic partition function, q_e , will be taken equal to only the nuclear spin statistical weight, g_n , for the molecule or complex under study.