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Homogeneous nucleation of water vapor in inert gas atmospheres

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HOMOGENEOUS NUCLEATION OF WATER VAPOR
IN INERT GAS ATMOSPHERES
by
ARTHUR HENRY BIERMANN, 1945-

A DISSERTATION
Presented to the Faculty of the Graduate School of the
UNIVERSITY OF MISSOURI-ROLLA

In Partial Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY
in
Engineering Physics
1971

James H. Keene Jr.
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August 1971
James L. Kassner, Jr., Dissertation Supervisor
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Abstract

The homogeneous nucleation of water vapor in atmospheres of helium, neon, argon, krypton, and xenon was studied using an expansion type cloud chamber. A strong dependence of the nucleation rate on the particular inert carrier gas was observed. At present the only dependence upon the nature of the carrier gas included in classical nucleation theories is a small factor arising from kinetic considerations which is in the wrong direction to explain the observations.

To explain the dependence of the rate on the nature of the carrier gas, a molecular cluster model is assumed allowing inert gas atoms to occupy the cavities in a clathrate-like structure. The envelopment of the carrier gas atoms in these cavities results in a substantial interaction energy. The law of mass action is applied to this hydration reaction to achieve the dependence of the nucleation rate on the nature for the carrier gas.

Since detailed computations were undertaken for only one cluster size, namely a 57 molecule four celled cluster, the results apply to only one supersaturation. The results
are in reasonable agreement with experiment considering the degree of approximation made in the computations. This work indicates further the power of molecular treatments to treat subtleties in the nucleation process which cannot be effectively handled by the classical theory.
ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to Dr. James L. Kassner, Jr., Director of the Graduate Center for Cloud Physics Research, for his assistance, advice, and motivation throughout this research.

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I. INTRODUCTION

Recently a renewed interest has occurred in the theory of nucleation phenomena. This is evidenced by the increase in the amount of literature on water condensation, droplet growth, and cloud formation. The simplest form of nucleation, homogeneous nucleation, still remains poorly understood and considerable controversy surrounds the proper development of the classical liquid drop formulation of the theory.

Homogeneous nucleation occurs in the absence of foreign particles, surfaces, ions, or other agents which serve to reduce the free energy barrier. Water phase transitions, which are blocked by a vapor to liquid free energy barrier, do not occur until a supersaturation of 4 or greater has been reached. This nucleation barrier arises from the fact that the surface to volume ratio is unfavorable for small pre-nucleation embryos so that the energy required to create new surface exceeds the bulk latent heat. Allen and Kassner\textsuperscript{1} have shown experimentally, and this author verifies, that homogeneous nucleation of water drops from the vapor is greater when argon is used as a noncondensible carrier gas than in the case of helium. In this work homogeneous nucleation experiments have also been made in several additional inert carrier gases, namely neon, krypton, and xenon.

Homogeneous nucleation measurements of supersaturated
vapors have been made with expansion cloud chambers,\textsuperscript{1-6} thermal diffusion chambers,\textsuperscript{7-9} nozzles,\textsuperscript{10-13} and nozzle beams.\textsuperscript{14,15} Katz and Ostermier have found generally good agreement between the classical nucleation theories and experimental results for ethanol, methanol, hexane, and water. Courtney has found that condensation of water vapor at high temperatures like 260°K could also be explained by the classical theories with a small accommodation coefficient, however nucleation at lower temperatures was considerably faster than predicted. Recent nozzle experiments\textsuperscript{8} indicate that the nucleation rate of water vapor is in agreement with the classical theories, while NH\textsubscript{3} nucleation occurs at much higher rates as predicted by the Lothe-Pound theory. Hence, the experimental nucleation data adds to the controversy between the Lothe-Pound and classical theories.\textsuperscript{16}

The classical liquid drop theory, as developed by Farkas,\textsuperscript{17} Volmer,\textsuperscript{18} Becker and Doring,\textsuperscript{19} Frenkel,\textsuperscript{20} and others does not contain a dependence on the nature of carrier gas in the nucleation rate expression. A non-thermal correction factor due to kinetics proposed by Feder, et. al.,\textsuperscript{21} would cause the nucleation rate of water in helium to be higher than that in argon, the reverse of the experimental observations by Allen and Kassner.\textsuperscript{1} The cloud chamber employed by workers in this laboratory\textsuperscript{1,3,4} possessed more flexibility in its expansion mechanism and more sophisticated systems for accurately measuring the thermodynamic
parameters than has been previously employed. Thus, more detailed information has been obtained on a given nucleating system. In addition to the dependence upon the nature of the noncondensible gas, Allen and Kassner also observed a decided inflection in the curve representing the log of the droplets nucleated* versus increasing peak supersaturation. This feature was further explored experimentally by measuring the nucleation rate as a function of increasing sensitive time;\(^1,3\) the nucleation rate was found to decrease with increasing time roughly exponentially which was believed by Allen and Kassner to be the result of heterogeneous nucleation where a single reactive molecule (perhaps hydrogen peroxide) helps stabilize the pre-nucleation cluster. Allen and Kassner\(^1\) believed a molecular model would be better adapted to taking into account these features which are characteristic of water vapor nucleation.

Bolander, Kassner, and Zung\(^22\) undertook the development of a molecular model for the nucleation of water vapor. This work has been extended by Daece, Lund, Plummer, Hale, and Kassner.\(^23\) In order to introduce the correct dependence on the carrier gas, the molecular model is extended so that the embryo structure allows the carrier gas atoms an opportunity to occupy the interstitial space in the

*The droplets nucleated times 100 gives the nucleation rate at the peak supersaturation.
pentagonal dodecahedral clathrate cages composed of water molecules. The envelopment of carrier gas atoms in these cavities gives rise to a substantial interaction energy which provides the physical mechanism proposed in this work for the dependence of the nucleation rate on the nature of the carrier gas.
II. CLOUD CHAMBER PROCEDURE

Through its 90 years of existence, the Wilson expansion cloud chamber has played a very important role in nuclear physics which has completely overshadowed its role in atmospheric physics. The very first research was done by Aitken and C.T.R. Wilson\textsuperscript{24} in their attempts to simulate cloud formation in the laboratory. The Wilson type expansion cloud chamber used in this laboratory was initially developed for cosmic ray studies. Nucleation experiments were begun in 1962 when the updated chamber facility was completed. It has been used and improved upon by Allard,\textsuperscript{25} Packwood,\textsuperscript{26} Grayson,\textsuperscript{27} Schmitt,\textsuperscript{28} Dawbarn,\textsuperscript{29} Smith,\textsuperscript{30} Allen,\textsuperscript{31} and White.\textsuperscript{32} The cloud chamber facility is extremely flexible and has been used to study a variety of condensation phenomena. A drawing of the cloud chamber is shown in Fig. 1. The most significant feature of the chamber is that the piston position is determined by the quantity of air remaining in the lower chamber. Expansion or compression ratios are determined by the amount of air released from or injected into the lower pneumatic chamber. This type of operating system adds great flexibility to the apparatus.

For homogeneous nucleation rate measurements, the chamber is programmed as shown in Fig. 2. The pre-expansion
Fig. 1. The Cloud Chamber
Fig. 2. The Cloud Chamber Cycle
pressure is indicated by A, typically 1200 mm Hg. During this time, an electrostatic clearing field of 80 volts/cm sweeps out any ions which could result in heterogeneous nucleation on ions. BC is the fast expansion, capable of reaching supersaturation ratios as high as 7. A short compression, EF, terminates the nucleation process. The sensitive time, DCEF, may be varied from .01 to 1 second before heat flow from the walls appreciably disturbs the sensitive volume. The thermal diffusion profiles as a function of time and radius for the wall effect of this chamber for a helium carrier gas are displayed by Allen and Kassner.\textsuperscript{31} This indicates that conditions in the center of the chamber remain known to within $\pm 0.1^\circ\text{C}$ for about one second after the expansion. This time is longer for gases with lower thermal conductivities. The nucleation portion of any experiment must be completed within about one second. FG allows time for droplets to grow to photographable size at a suitably large supersaturation. A one centimeter thick horizontal beam of light is produced by two light boxes containing a cylindrical xenon flash lamp collimated by cylindrical strip lenses. The narrow beam defines the observed volume through the center of the chamber. GH is a recompression to the overcompressed level HI that is required to counterbalance the heat flow into the chamber caused by the expansion. After I, the chamber returns to the initial pre-expansion state. The total
cycle requires 4-5 minutes. BDF demonstrates a cleaning type expansion; generally a supersaturation of less than 3.9 is attained. Two such expansions are used between each data expansion to insure that all re-evaporation nuclei have been eliminated.

Normally the cloud chamber is flushed with a particular carrier gas many times before a set of data is taken. This technique is wasteful, but allowable when inexpensive commercial grade gases such as helium and argon are used. The more expensive gases, neon and especially xenon and krypton, must not only be conserved but retrieved. To fill the cloud chamber with one of the more expensive carrier gases, the volume below the piston is evacuated, holding the piston in a fully expanded position. Then the dry cloud chamber sensitive volume is evacuated. Finally, the carrier gas and water are allowed to repressurize the chamber. For retrieval the gas is passed out through two dry ice cold traps to remove the bulk of the water vapor and into its original tank which is cooled to liquid nitrogen temperatures so that either xenon or krypton, as the case may be, will condense in the original container.

The water used in the sensitive volume is purified through a double distilling system, the second stage being a Corning glass still. More elaborate purification techniques for water have been shown not to alter nucleation results.
The most critical measurement to be made in this type of nucleation experiment is that of the pressure. A pressure transducer is used to measure the initial pressure and the pressure is monitored continuously around the CDEF region shown in Fig. 2. The output is displayed on a light beam oscillograph during appropriate portions of the chamber cycle. A new pressure calibration is obtained for each carrier gas since the different thermal diffusion coefficients change the operating temperature of the strain gauge type pressure transducer and thereby change its calibration slightly. The initial temperature is read from a thermocouple inside the cloud chamber. With the above three readings, the Beattie-Bridgman equation of state for the noncondensible gas,33 and the specific heat capacity and compressibility for water, the final temperature and supersaturation can be calculated.
III. EXPERIMENTAL RESULTS

The author has observed the droplet densities formed by the homogeneous nucleation of liquid water droplets from the vapor in atmospheres of helium, neon, argon, krypton, and xenon for cloud chamber expansions of the form shown in Fig. 2. In addition to these some data was obtained after deliberate contamination of the water with hydrogen peroxide. Most of the drop densities are plotted versus the peak supersaturation occurring in the narrowest pressure pulse.

For extremely short nucleation pulses, the pressure versus time pulse is very nearly parabolic. Strictly speaking the nucleation rate should be integrated throughout the pulse and compared with the total number of droplets observed for that particular experiment. However, since the bulk of the total number of droplets form at the very highest supersaturation attained (Fig. 3), it is reasonable to plot the total number of droplets nucleated as a function of peak supersaturation. This information is readily converted to nucleation rates by a simple conversion which is explained next. Due to the manner in which the cloud chamber is operated, the shape of the pressure versus time pulses are very uniform and a characteristic sensitive time can be readily assigned for the
Fig. 5. Nucleation Pulses for $S = 5.90$
$T = 267.7^\circ K$
Total drops nucleated = 19.
conversion from drop counts to nucleation rates. This
can be accomplished for the case of the forced compression,
LF in Fig. 2, with some degree of certainty whereas it
cannot be done with a reasonable degree of certainty for
cloud chambers employing a "natural" sensitive time which
is terminated only by wall effects and the latent heat
liberated through droplet growth. After several such
nucleation pulses were analyzed it was found that the
conversion from drop count density to nucleation rate is
very close to 100 throughout the supersaturation range of
4-6.5.

The author's argon, neon, and helium data is presented
in Fig. 4. The curves are least squares fits for the num-
ber of drops per cc. experimentally observed for a given
supersaturation with a pre-expansion temperature of 25°C
and an initial pressure of 1200 mm Hg. The argon and
helium data agree very favorably with that obtained by
Allen three years previous. Fig. 5 shows the comparison;
it should be noted that Allen's counts were taken with a
pre-expansion temperature of 22.5°C. Also the inflection
in the curves, thought by Allen and Kassner to be caused
by a form of heterogeneous nucleation, for which the
centers are rapidly depleted,¹ is reproducible. However,
the inflection found by the author for helium is not as
pronounced as that found by Allen.

The xenon and krypton data is shown in Fig. 6.
Fig. 4. Argon, Neon, Helium Data.
Fig. 5. Comparison to Allen's Data.
Fig. 6. Krypton and Xenon Data.
Because of the limited amount of xenon gas available, the initial pressure used with xenon in the chamber was only approximately 1040 mm Hg. This is evidenced by the lower effective adiabatic index in Table I.

The krypton used in the experiment was apparently slightly radioactive, for tracks caused by ions were visible to such an extent as to ruin chances of a homogeneous nucleation drop count when the clearing field was switched "off" during the sensitive time. Therefore, the clearing field was left "on" throughout the expansion to remove all the ions possible. This made possible reliable drop counts above 5 drops per cc. Hence, the lower part of the krypton least squares fit is extrapolated.

In addition to the narrow pulse, the sensitive time was varied. For neon, results are shown in Fig. 7. This enables the rate of decay of the nucleation rate with respect to time to be determined in the region below the inflection. It was not feasible to carry out this sort of experiment above the inflection point because the drop densities became too large too quickly.

Because of curiosity in the nature of the phenomenon responsible for the inflection in the curves, two side experiments were attempted. The first was to introduce a pint of 30 percent hydrogen peroxide solution into the approximately one and one-half gallons of water in the bottom of the chamber. Rate measurements were taken
<table>
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<th>Gas</th>
<th>(\gamma)</th>
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<tr>
<td>Helium</td>
<td>1.6567</td>
</tr>
<tr>
<td>Neon</td>
<td>1.6572</td>
</tr>
<tr>
<td>Argon</td>
<td>1.6573</td>
</tr>
<tr>
<td>Krypton</td>
<td>1.6540</td>
</tr>
<tr>
<td>Xenon</td>
<td>1.6527</td>
</tr>
</tbody>
</table>

TABLE I.

Effective Adiabatic Index, \(\gamma\)
for \(T_1 = 25.0^\circ C\), \(S = 5.05\)
Fig. 7. Decay of Nucleation Rate with Neon as the Carrier Gas.
immediately for, of course, the hydrogen peroxide was decomposing into water and oxygen. The result (Fig. 8) indicated that hydrogen peroxide or its decomposition products can be a suspect as a source for neutral nucleation centers for water nucleation, because a pronounced increase in the nucleation rate was observed. The second experiment involved bombarding the cloud chamber with a dense beam of x-rays immediately prior to expansion. Although an increase of approximately a factor of two was noticeable in some drop counts at higher supersaturations, differences were not observed at lower supersaturations. It is probable that the heavy x-ray dosage also caused the formation of some neutral excited gas atoms which acted as condensation centers in the following expansion.

In conclusion, it should be realized that the drop densities have probable errors of 10 percent resulting from the drop count alone. The long range reproducibility of the data using helium and argon as the noncondensible gases is better than anticipated\(^1\) and indicative of the precision with which this cloud chamber can operate. With regard to the inflections appearing in all the curves, one can note that the least predominant inflection occurs using the carrier gas of helium while the most significant inflection occurs with xenon.

The data exemplifies that the nucleation rate should contain a dependence on the noncondensible gas in a
Fig. 8. Hydrogen Peroxide Data.
direction opposite to that predicted by the appropriate kinetics. An explanation is sought in an extension of the molecular theory\textsuperscript{23} where a clathrate-like model for the pre-nucleation embryos is assumed which allows several noncondensible gas atoms to occupy the cavities in the clathrate cages. The resulting interaction energies of these hydrates alter the nucleation rate for the water vapor in the various inert gas atmospheres.
IV. THEORY

Introduction. Previous developments of classical homogeneous nucleation theory do not allow for the inclusion of noncondensable gas atoms within the pre-nucleation clusters. It has been established that the homogeneous nucleation rate of water droplets is higher in argon than in helium by an amount too large to be explained by depletion of supersaturation and by appropriate differences in gas kinetics.\textsuperscript{21} Efforts by Bolander, Kassner, and Zung\textsuperscript{22} and Daee\textsuperscript{34} using dodecahedra clathrate-like cluster models have led to the development of a molecular model for the nucleation of water from the vapor. The resulting free energy of formation is no longer smooth as predicted by classical theory, but exhibits minima corresponding to the completion of closed cages for the cluster structures. Similarly in this work the interstices in the dodecahedral cages of the model are allowed to be occupied by inert gas atoms. To understand the effect of a change in the energy of formation of the cluster due to the inclusion of an inert gas atom, a review of the classical theory of homogeneous nucleation is in order.

Review of Literature. The classical homogeneous nucleation theory based on the liquid-drop model assumes the condensing water drops are spherical in shape and possess bulk
liquid characteristics. The energy of formation is described by assigning macroscopic thermodynamic properties to the cluster, a questionable procedure when dealing with clusters containing less than 100 water molecules. One of the underlying fundamental relations used in the theory of homogeneous nucleation is the Thomson-Helmholtz equation which gives the vapor pressure over curved surfaces,

$$\ln \frac{p}{p_\infty} = \frac{2\sigma v}{rKT}$$  \hspace{1cm} (1)$$

where \(p/p_\infty\) = ratio of the pressure over a curved surface to that over a plane surface and

- \(\sigma\) = specific surface free energy
- \(v\) = molecular volume of the liquid
- \(r\) = radius of curvature
- \(k\) = Boltzman's constant
- \(T\) = absolute temperature.

Kuhrt modified the Thomson-Helmholtz relation to include a term arising from the translation and rotation of the molecules for free clusters of small radius and obtained

$$\ln \frac{p}{p_\infty} = \frac{2\sigma v}{rKT} - \frac{4}{g}$$  \hspace{1cm} (2)$$

where \(g\) is the number of water molecules. Nucleation theories are based on the calculation of the change in the Gibbs or Helmholtz free energies when a cluster increases or decreases in size. For the classical result using
the liquid drop model in theories like Volmer,\textsuperscript{18} Becker-Doring,\textsuperscript{19} and Frenkel,\textsuperscript{20} this energy change amounts to the difference between the surface and the volume energy terms

\[ \Delta G = -\frac{4\pi r^3 kT \ln S}{3\nu} + 4\pi r^2 \sigma \]  

(3)

where \( S \) is the supersaturation, \( r \) is the cluster radius, and \( \sigma \) is the surface tension. The radius may be expressed as a function of \( \mu \) using the relation

\[ \frac{4\pi r^3}{3} = \nu \mu \]  

(4)

Eliminating \( r \) from Eq. (3),

\[ \Delta G = -g kT \ln S + 4\pi \sigma \mu^{2/3} \mu^{2/3} \]  

(5)

where \( \mu = \frac{3\nu}{4\pi} \). By setting the partial derivative of \( \Delta G \) with respect to \( r \) equal to zero, the critical drop radius is obtained,

\[ r^* = \frac{2\sigma \nu}{kT \ln S} \]  

(6)

and the corresponding maximum energy change is

\[ \Delta G^* = \frac{16\pi \sigma^3}{3} \left[ \frac{\nu}{kT \ln S} \right]^2 \]  

(7)

The critical radius is the size of a drop whose probability of condensing further or evaporating is equal. \( \Delta G^* \) is the energy barrier which the embryo must surmount in order to become free growing. This energy enters into the rate through a Boltzman distribution function in
determining the concentration of the drops of size $r^*$:

$$n_{r^*} = n_1 e^{-\frac{\Delta G^*}{kT}}$$  \hspace{1cm} (8)

where $n_1$ is the concentration of the monomers. Much controversy arises in the pre-exponential factor (Eq. 9) which is usually developed from kinetic theory. Often this term includes the Zeldovich correction factor, $Z$, which is a correction due to the integration over cluster size, $g$. Combining these factors, the nucleation rate becomes

$$J = \alpha A^* \beta Z n_1 e^{-\frac{\Delta G^*}{kT}}$$  \hspace{1cm} (9)

where $\beta$ = the impingement frequency of monomers on a flat surface, or $p/(2\pi mkT)^{1/2}$

$p$ = the water vapor pressure

$A^*$ = the surface area of the critical cluster

$$Z = \left[ -\frac{1}{2\pi kT} \frac{\partial^2 \Delta G}{\partial g^2} \right]_{g^*}^{1/2}$$

$\alpha$ = the accommodation coefficient.

The classical rate may also be expressed as a summation,

$$J = \left[ \sum \frac{1}{S g n_g} \right]^{-1}$$  \hspace{1cm} (10)

which is obtained from solving the following set of differential equations:

$$\frac{dn_g}{dt} = k g n_1 n_{g-1} - k g n_1 n_g - r g n_g + r g+1 n_{g+1}$$  \hspace{1cm} (11)
using the steady-state condition that $\frac{dn_g}{dt} = 0$, where

$n_g$ = the concentration of clusters having $g$ molecules and

$k_g, r_g$ = the specific rate constants for the formation and
dissociation of the $g$ size cluster.

Various nucleation rates have been tested and compared
to the author's helium data for 25.0°C (Fig. 9). The
number of drops which would be formed by assuming classical
nucleation rates of Becker-Doring and Frenkel is seen to
be approximately a factor of 100-1000 higher than the data
above the inflection; there is exceptionally close agree-
ment below the inflection point if one could discount the
exponential decay with increasing sensitive time which is
exhibited in this region. The accommodation coefficient
would have to be less than .01 to obtain a reasonable fit
to experiment above the inflection. A rate law proposed
by Abraham\textsuperscript{42} using Band's theory\textsuperscript{43} for an imperfect vapor
predicts rates which are too low. A nucleation rate law
developed by White\textsuperscript{32} for nucleation on ions can be used for
homogeneous nucleation if the ion terms are omitted. His
rate law is obtained by adding a dipole-dipole correction
to $\Delta G^*$,\textsuperscript{44,45} caused by the pre-nucleation embryos having
an orientated dipole surface layer and resulting in an
overall increase in the critical cluster size (Fig. 10).
Choosing an oxygen-oxygen bond length of 3.0 angstroms, a
fit to the data is shown. The inflection results from
allowing a heterogeneous component to be superimposed on
the homogeneous nucleation rate to provide depletion as
Fig. 9. Comparison of some nucleation theories.
Fig. 10. Critical Cluster Size.
proposed by Allen and Kassner.\textsuperscript{1}

The Lothe-Pound rate law,\textsuperscript{46} renowned for its $10^{17}$
factor above classical rates, can be lowered by assuming a
surface tension correction of the form $\sigma = \sigma_0 + A/4\pi r^2$.\textsuperscript{44}
None of these nucleation rates, except the latest Lothe-
Pound correction\textsuperscript{21} to their rate, depend on the type of
carrier gas present. This Lothe-Pound correction for the
carrier gas arises from the difference in mass and specific
heat of various gases. This pre-exponential factor causes
the argon rate to be approximately half that of helium, the
reverse of what is observed experimentally. Table II lists
this factor for the various inert gases. This pre-exponen-
tial factor is $b^2/(b^2 + q^2)$, where

$$b^2 = (c_v + \frac{k}{2})kT^2 + \frac{\beta}{\beta_c}(c_{v,c} + \frac{k}{2})kT^2,$$  \hspace{1cm} (12)

$q^2 = (9.29 \times 10^{-13} - 6.67 \times 10^{-16}T)$ erg/molecule
and $c_v =$ specific heat for the vapor
$c_{v,c} =$ specific heat for the carrier gas
$\beta, \beta_c =$ the respective impingement frequencies.

\textbf{Cluster Theory.} An intense effort has evolved within the
Graduate Center for Cloud Physics Research to develop a
more nearly molecular model for the nucleation of water
vapor. This was first suggested by the nature of the
experimental results obtained by Allen. Bolander, Kassner,
and Zung\textsuperscript{22} laid out the general features of the model and
carried out computations on the dimer. The work has been
<table>
<thead>
<tr>
<th>Gas</th>
<th>$\frac{b^2}{b^2 + q^2}$</th>
<th>Ratio to Helium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>.332</td>
<td>1.</td>
</tr>
<tr>
<td>Neon</td>
<td>.185</td>
<td>.557</td>
</tr>
<tr>
<td>Argon</td>
<td>.141</td>
<td>.425</td>
</tr>
<tr>
<td>Krypton</td>
<td>.104</td>
<td>.313</td>
</tr>
<tr>
<td>Xenon</td>
<td>.074</td>
<td>.223</td>
</tr>
</tbody>
</table>
extended by Daee\textsuperscript{34} who has calculated the free energy of formation for clusters ranging in size from 16 to 57.

The molecular theory assumes that clustering proceeds as water molecules hydrogen bond together. The hydrogen bond energy is about 10 times kT near room temperature so the cluster maintains a definite cluster structure between successive collisions with external molecules. Cluster models are required to conform closely to the tetrahedral coordination requirements of the water molecule, to maximize the number of bonds and to maximize the spherical symmetry. Pauling's\textsuperscript{47} clathrate-like structure (Fig. 11a) presents a particularly favorable type structure for the gas phase pre-nucleation cluster. The extension to this theory, presented in this work, allows for carrier gas atoms to occupy the interstitial cavities in the clathrate dodecahedral cages. The polar-nonpolar interaction with twenty surrounding molecules (in the case where inert gases are employed as the noncondensible gas) serves to change the free energy of formation of the cluster.

To calculate the interaction energy of the inert gas atom in such a cavity, a polar-nonpolar potential is used, the polarizability of the different inert gases being different. The following intermolecular potential is used:

\[
V = 4\varepsilon\{ (\sigma/r)^{12} - (\sigma/r)^6 \} - \frac{\mu_\sigma^2}{2r^6} (1+3\cos^2\theta) - \frac{6\mu_\sigma Q \cos^5\theta}{r^7} \tag{13}
\]

where \( r \) = distance between the centers of the gas atom
and the water molecule

\[ \mu = \text{dipole moment of the water molecule} \]

\[ Q = \text{quadrupole moment of the water molecule} \]

\[ \alpha = \text{polarizability of the gas atom} \]

\[ \theta = \text{angle between } r \text{ and the dipole direction of the water molecule.} \]

The potential parameters are calculated using

\[ \sigma = 0.5(\sigma_n + \sigma_p) X^{-1/6} \quad \varepsilon = a X^2 \]

where

\[ X = 1 + \frac{\alpha \mu^2}{4\alpha \sigma_n^3 \sigma_p^5} \quad \text{and} \quad a = (\varepsilon_n \varepsilon_p)^{1/2}. \]

\( \varepsilon_p \) and \( \sigma_p \) are the Lennard-Jones parameters for water and \( \varepsilon_n \) and \( \sigma_n \) the parameters for the inert gas.

The Lennard-Jones parameters and polarizabilities used in this work are listed for the various gases in Table III. The first term in Eq. (13) is the Lennard-Jones potential with the typical \( r^{-12} \) repulsive term and the \( r^{-6} \) attractive term. The second and third terms result from induction forces from the dipole and quadrupole of the polar water molecule, and are proportional to the polarizability of the gas atom. The quadrupole term accounts for only one percent of the total interaction energy and may be neglected for our purposes. The models were constructed by allowing each water molecule to participate in as many as four tetrahedrally arranged bonds, each bond having one hydrogen atom between the two oxygen atoms.
Fig. 11. Cluster Models.
TABLE III.

Lennard-Jones Parameters and Polarizabilities

<table>
<thead>
<tr>
<th></th>
<th>( \varepsilon/k ) (°K)</th>
<th>( \sigma ) (Å)</th>
<th>Polarizability, ( \alpha ) (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>380.</td>
<td>2.65</td>
<td></td>
</tr>
<tr>
<td>Helium</td>
<td>10.22</td>
<td>2.576</td>
<td>.204</td>
</tr>
<tr>
<td>Neon</td>
<td>35.7</td>
<td>2.789</td>
<td>.392</td>
</tr>
<tr>
<td>Argon</td>
<td>124.</td>
<td>3.418</td>
<td>1.630</td>
</tr>
<tr>
<td>Krypton</td>
<td>190.</td>
<td>3.61</td>
<td>2.465</td>
</tr>
<tr>
<td>Xenon</td>
<td>229.</td>
<td>4.055</td>
<td>4.010</td>
</tr>
</tbody>
</table>
This gives rise to the O-H...O bond with its disputed bond length and energy.\textsuperscript{50,51} There are numerous possible ways in which the dipoles can be arranged in a given clathrate structure due to the different possible orientations of the individual water molecules which satisfy the bonding requirements. Three various combinations of dipole orientations were tried, which exhibited negligible differences in the total interaction energy. The resultant interaction energies are listed in Table IV for an inert gas atom occupying a cavity in the 20 molecule dodecahedron. The interaction energy for a water molecule to occupy the dodecahedral cavity which includes the dipole-dipole, dipole-induced dipole, and polarization potentials is $0.52 \times 10^{-12}$ ergs or 0.32 eV. This is equivalent to an argon atom in the cluster except that the concentration of noncondensable gas molecules is approximately 50 times that of water monomers. Also it seems energetically more probable that the water molecule would bond into the cluster structure than reside as a non-hydrogen bonded monomer in the clathrate cavity.

The inert gas atoms with larger polarizabilities occupying the clathrate cavity cause the cluster to shrink slightly. The water-water bond length is allowed to vary to determine the minimum potential of the whole cluster as it would relax under the influence of the inert gas atom; that is,
### Table IV.

**Interaction Energies and Force Constants**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Interaction Energy (ergs)</th>
<th>Force Constant (dynes/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>(-0.83 \times 10^{-12})</td>
<td>(0.88 \times 10^4)</td>
</tr>
<tr>
<td>Neon</td>
<td>(-0.222)</td>
<td>(0.158)</td>
</tr>
<tr>
<td>Argon</td>
<td>(-0.510)</td>
<td>(0.248)</td>
</tr>
<tr>
<td>Krypton</td>
<td>(-0.724)</td>
<td>(0.290)</td>
</tr>
<tr>
<td>Xenon</td>
<td>(-0.995)</td>
<td>(0.278)</td>
</tr>
</tbody>
</table>
where \( \vec{n} \) is a unit normal in the direction of \( r \) and \( \vec{p}_1, \vec{p}_2 \) are the dipole directions. The first term is the Lennard-Jones potential for the water-water interactions, the second is the dipole-dipole water interaction, and the third is the polar-nonpolar interaction from Eq. (13). Resulting curves are shown for xenon, the extreme case, in Fig. 12. Without the polar-nonpolar term the cluster not containing a gas atom has a minimum potential at a bond length of 2.77 angstroms.

Critical cluster size for various rate laws is shown as a function of supersaturation in Fig. 10. A typical cluster size then is composed of three or four clathrate cages as shown in Fig. 11b, some or all of which might be occupied with an inert gas atom. The exact structure used in this computation is a 57 molecule, four cage cluster. In fitting four dodecahedra together some deformation from perfect tetrahedral coordination is expected. The structure is allowed to relax and a certain amount of strain is introduced in the bonds. The relaxation position of the 57 molecules was chosen by assuming the water-water interaction can be approximated by two harmonic oscillator type potentials. The total potential is then

\[
V = \frac{1}{2} k_r \sum (r_i - r_0)^2 + \frac{1}{2} k_\theta \sum \theta_i \theta_0 \sum^2 \left( \theta_i - \theta_0 \right) \left( \theta_i - \theta_0 \right)
\]

where \( r_i = \text{distance between two adjacent water molecules} \).
Fig. 12. Cluster Relaxation Involving a Xenon Atom.
\[ \theta_i = \text{angle between any three water molecules} \]
\[ r_0, \theta_0 = \text{the equilibrium values.} \]

Minimization of this potential yielded the various critical bondlengths and angles, or simply the coordinates of the water molecules in the cluster. The strain energy introduced by this relaxation amounted to 0.04 eV or 1.7 kT.

From the moments of inertia, \( I_1 = 4268 \times 10^{-40}, I_2 = 4268 \times 10^{-40}, I_3 = 4000 \times 10^{-40} \text{ gm cm}^2 \), one can see the resulting structure is quite spherically symmetric; using \( I = \frac{2}{5} m r^2 \) in the spherical classical liquid drop model and the average radius of the relaxed cluster, a simple calculation predicts 59 molecules for this sized cluster. Hence, this molecular cluster model is only slightly less dense than that predicted by the classical liquid drop model.

The law of mass action can be used to approximate the concentrations of clusters containing a given number of gas atoms. Consider the following reaction:

\[ A_g + nB \rightarrow (A_g \cdot nB) = C \quad (16) \]

where \( A_g = \text{a water cluster having } g \text{ molecules,} \)
\( B = \text{the inert gas atom, and} \)
\( C = \text{the resulting hydrate.} \)

Applying the law of mass action, the concentration of C is given:

\[ \rho_C = \frac{\rho_A \rho_B^n (Q_C/V) e^{-\Delta E/kT}}{(Q_A/V) (Q_B/V)^n} \quad (17) \]
where \( \rho_A \) = the concentration of clusters having \( g \) water molecules,
\( \rho_B \) = the concentration of the inert gas atoms,
\( \Delta E \) = the energy change of the reaction, and
\( Q_A, Q_B, Q_C \) = the respective partition functions.

Evaluation of partition functions is accomplished by letting
\( Q = Q_t Q_r Q_v \) where \( Q_t, Q_r, Q_v \) are the translation, rotational, and vibrational partition functions. The translation part is easiest to evaluate and is evaluated first. Using
\[
Q_t = \left(2\pi mkT/h^2\right)^{3/2} V
\]
Eq. (17) becomes
\[
\frac{\rho_C}{\rho_A} = \frac{\rho_B^n (1 + nm_B/m_A)^{3/2}}{Q_{Ar} Q_{At} \left[(2\pi mkT/h^2)^{3/2}\right]^n} Q_{Cr} Q_{Ct}
\] (18)

The rotational parts can be calculated by assuming a given cluster model and the number of cavities occupied by the gas atoms.

\[
Q_r = 8\pi^2 \left(2\pi kT\right)^{3/2} \left(I_1 I_2 I_3\right)^{1/2} /\sigma h^3
\]

Such a calculation requires the principal moments of inertia, \( I_1, I_2, I_3 \) and the rotational symmetry number \( \sigma \) and is highly dependent on the geometry. However, the same geometry is used for comparing the effect of the different inert gases, and actually only the ratios of concentrations are of interest. Hopefully, errors tend to cancel in this procedure.
The vibrational partition functions are the most complicated to evaluate. The vibration partition function is

\[ Q_v = \prod_i \frac{e^{-\hbar \nu_i / 2kT}}{1 - e^{-\hbar \nu_i / kT}} \]  

where \( \hbar \) is Planck's constant, \( g \) is the number of water molecules in the cluster, and \( \nu_i \) are the internal vibration frequencies. The hydrogen bonded water molecules in these clathrate structures are treated as harmonic oscillators to a first approximation. Using a given cluster structure, the solution to the vibration spectrum is a large normal mode problem. A series of computer programs, by Schachtschneider, was extremely helpful, not only in determining these vibration frequencies, but also the coordinates of the water molecules in the cluster. Both stretching and bending forces are allowed between the water molecules, but only stretching is considered between the inert gas atom and the surrounding water molecules. The stretch force constant for the latter interaction is determined from the polar-nonpolar potential. These force constants for argon and krypton are about one-tenth of the stretch force constant between two water molecules (Table IV). The values used for the stretching and bending force constants between two water molecules are \( .19 \times 10^5 \) and \( .045 \times 10^4 \) dynes/cm respectively. When an inert gas atom is added in a cavity, it is found that the lower vibration modes are shifted upward while the higher modes remain
essentially unchanged. In Fig. 13 the frequency spectrum of the relaxed 57 molecule water vapor cluster is compared to the same structure with four argon atoms enclosed. Intramolecular vibrations and librations are neglected. This is a good approximation since one expects their effect to cancel when the ratio of the concentrations is calculated.

So far, it has been assumed that the O-H...O bond energy is a constant when adding a gas atom in one or more of the interstices. However, this is not valid, especially in the cases of xenon and krypton where the polarizability is considerably greater. Although undoubtedly the bond energy is a very smooth function with respect to the bond length, even a small change in its energy is perceptible when there are 30 to 94 bonds involved. The total bond energy can be calculated using

\[ E_B = 2n_4E_{B4} + \frac{3}{2} n_3E_{B3} + n_2E_{B2} + \frac{1}{2} n_1E_{B1} \]

where \( E_{Bn} = [1+\epsilon(n-1)]E \), \( n_i \) = the number of molecules having \( i \) bonds, and \( \epsilon = 0.062 \) and \( E = -6.1 \text{ kcal/mole} \). Then the total partition function must include the bond energy.

\[ Q_T = Q_tQ_PERSONAL_1Q_v e^{E_B/kT} \]

The theory allowing no bond energy shift, Eq. (18), would predict krypton above argon, and xenon far above krypton. However, to bring both krypton and xenon nucleation rates into or below the argon nucleation rate curve
Fig. 13. Comparison of Normal Vibration Frequencies.
requires changing the bond energy only from 6.1 to 5.94 kcal/mole for the case where only one cavity is occupied; i.e., there are only 30 affected bonds. Some of the ratios of concentrations $\rho_C/\rho_A$ which have been calculated are listed in Table V. These concentrations do not include the non-isothermal kinetic factor of Table II. This factor is negligible for neon and argon in relation to helium and would only slightly alter the bond energy adjustment made for krypton and xenon. The xenon and krypton figures include a bond energy shift to 5.94 and 6.04 kcal/mole respectively. One could explain the further reduction in the nucleation rate seen with xenon as the noncondensible gas at higher supersaturations by realizing the critical cluster size decreases and hence, any bond energy shift would cause proportionally a larger effect in the free energy.

It should be realized that in this work only one cluster model has been investigated and therefore the results are valid at only one supersaturation. Depending on the theory chosen, as in Fig. 10, this supersaturation ratio is in the range of 5 to 6. Qualitatively then from these concentrations it can be seen that nucleation rates are least affected by the occlusion of helium or neon atoms in the cluster, most affected by argon, and then xenon and krypton depending on the bond energy. Hence, the molecular theory not only predicts shifts in the nucleation rates due to occlusion of noncondensible inert
TABLE V.

Free energies and concentration ratios for the 57 molecule cluster having 1 gas atom. Also listed are the gas solubilities in water.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Free Energy (ev)</th>
<th>$\rho_C/\rho_A$</th>
<th>Solubilities **</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>-32.57</td>
<td>1.</td>
<td>-</td>
</tr>
<tr>
<td>Helium</td>
<td>-32.62</td>
<td>.000066</td>
<td>9.78</td>
</tr>
<tr>
<td>Neon</td>
<td>-32.72</td>
<td>.000341</td>
<td>14.0</td>
</tr>
<tr>
<td>Argon</td>
<td>-32.88</td>
<td>.268</td>
<td>52.4</td>
</tr>
<tr>
<td>Krypton</td>
<td>-32.92</td>
<td>6.0, .2 *</td>
<td>99.1</td>
</tr>
<tr>
<td>Xenon</td>
<td>-32.94</td>
<td>850.0, .2 *</td>
<td>203.2</td>
</tr>
</tbody>
</table>

* Bond energy adjusted.

** Given in cc of gas per 1000 gm of water with a temperature = 0°C and a gas pressure = 760 mm.
TABLE VI.

Free energies and concentration ratios for the 57 molecule cluster having 1 or more argon atoms

<table>
<thead>
<tr>
<th>Number of argon atoms</th>
<th>Free Energy (ev)</th>
<th>$\rho_C/\rho_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-32.88</td>
<td>.268</td>
</tr>
<tr>
<td>2</td>
<td>-33.17</td>
<td>.02</td>
</tr>
<tr>
<td>3</td>
<td>-33.44</td>
<td>.001</td>
</tr>
<tr>
<td>4</td>
<td>-33.70</td>
<td>.00002</td>
</tr>
</tbody>
</table>
gas atoms but the magnitudes of the shifts are reasonable considering the shortcomings which still exist in the theoretical treatment.

**Inflections.** The interesting inflections in the nucleation rate data which have been observed in this laboratory since nucleation measurements have been made can be explained by assuming the presence of a heterogeneous nucleating agent.\(^1\) Temperature dependence studies by Allen and Kassner have shown that the concentration of the heterogeneous nucleating agent seems to vary in approximate proportion to the saturation vapor pressure of the water in the chamber before the expansion. It would seem most likely that the heterogeneous nucleating agent is neutral. For an example, it has been suggested by Burke\(^55\) that hydrogen peroxide could be produced by irradiation through the following series of reactions:

\[
\begin{align*}
M & \rightarrow M^* \\
M^* + H_2O & \rightarrow M + H + OH \\
M^* + H_2O & \rightarrow M + H_2O^+ + e \\
H + OH & \rightarrow H_2O \\
H + H & \rightarrow H_2 \\
OH + OH & \rightarrow H_2O_2
\end{align*}
\]

where \(M^*\) is an excited gas atom. It has been shown experimentally by this author that hydrogen peroxide could be just such a neutral nucleating agent.

An alternative explanation to the inflections is
provided by the molecular cluster theory itself. The existence of maxima and minima in the free energy of formation due to the cluster structure\textsuperscript{23} gives rise to minima and maxima respectively in the cluster concentrations. As the supersaturation increases the portions of the free energy curve representing larger cluster numbers, \( g \), fall faster than do those representing smaller cluster numbers, as shown in Fig. 14. This would allow a nonsteady-state build-up of clusters at the free energy minima which in turn could be dumped into the nucleation process as the supersaturation is further increased. At suitably high supersaturations this excess population of clusters would be depleted and the nucleation rate would return to a lower value representative of a flow of clusters from farther back down the free energy curve, i.e., smaller cluster sizes. Hence, the heterogeneous component as explained by Allen and Kassner could be a manifestation of an excess of pre-nucleating clusters resulting from a population inversion caused by the effect of cluster structure on the free energy curve.

Such maxima and minima in the free energy of formation have also been calculated theoretically by Burton\textsuperscript{56} for argon clusters. Burton has found that the slope in the nucleation rate decreases with increasing supersaturation ratios more than is predicted by the classical liquid drop theory. The calculation requires using the steady state nucleation rate expression, Eq. (10), and therefore
Fig. 14. Free Energy having a Double Barrier.

$\Delta G =$ free energy of formation; $\ldots\ldots$ indicates the classical case.

$\ln N_g =$ logarithm of the concentration; $\ldots\ldots$ indicates the steady-state case and $\ldots\ldots$ indicates depletion of the population inversion.
may be questionable. The author tried this approach and found that although the nucleation rate tapers off at higher supersaturations, it does not recover as the data indicates. It appears clear that the steady-state approximation is not valid for nucleation processes exhibiting more than one barrier.

A thorough solution to the problem is to solve the exact time dependent equations, Eq. (11), using an other than classical free energy function. Computer programs exist for doing just this with the classical free energy, but computer time is very burdensome.\textsuperscript{57} If this procedure were attempted the hydration reaction, Eq. (16), could also be incorporated at various stages of the cluster formation and perhaps even the respective extent of the inflections for the various gases could be predicted. This would result in an additional set of differential equations specifying the concentration of the hydrated clusters to be solved along with the slightly modified nonsteady-state equations. Partition functions would still be needed for calculating the pertinent forward and reverse reaction constants. A quantitative result could then be achieved.
V. CONCLUSIONS

The experimental data has shown that the nucleation rate of water from the vapor is dependent on the carrier gas used. The nucleation rate of water with argon as the carrier gas is 3 to 10 times as great as using helium as the carrier gas. Although not proven, it is likely that the extent of the inflections in the rate curves correspond to the strength of the polar-nonpolar interaction energy between a particular gas atom and surrounding water molecules forming clathrate structures. The comparison of this cluster theory to the data can certainly only be used as a qualitative argument. Assumptions have included making harmonic oscillator potential approximations, the law of mass action, and neglecting interactions between clusters. Yet the use of this 57 molecule water vapor cluster model for one supersaturation does qualitatively predict the nucleation rate of water in argon to be higher than that observed in helium. In addition the neon data is predicted to be slightly above helium and the xenon, krypton data can be placed near the argon data by allowing the hydrogen bond energy to shift by 2 percent. This is most likely the result of the relaxation of the cluster under the influence of the foreign molecule. It is felt that this work further extends and strengthens the molecular theory of nucleation
of water droplets from the vapor by considering facets of the nucleation process for which the classical theory is powerless.
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VII. VITA

The author was born January 20, 1945, in Washington, Missouri. He graduated from Washington Public High School in 1963 and entered the University of Missouri at Rolla. There he received his B.S. in Physics in January, 1967, and his M.S. in Physics in June, 1969. Since 1967, he has been a doctoral candidate in the Graduate Center for Cloud Physics Research, University of Missouri at Rolla.

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