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Nucleation in supersaturated gaseous systems

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NUCLEATION IN SUPERSATURATED GASEOUS SYSTEMS

by

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Approved by

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H.M.S.

Boston, Massachusetts
May 1954
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II INTRODUCTION

One of the most strikingly general properties of matter in the fluid state is the existence, below a certain critical temperature, of a sharp phase transition representing condensation-evaporation. This development of non-homogeneity in an initially homogeneous phase is characterized on the $Pv$ isotherm by a horizontal portion, at the end points of which $v_s$ undergoes a discontinuous change. These points define the saturation specific volumes of the fluid.

The extreme generality of the phenomenon attracted much experimental and theoretical attention though the details of the kinetic process remained obscure. In the late 1800's, in the course of meteorological investigations relating to processes of cloud formation, it was discovered that a vapor need not condense when it is saturated. Under certain conditions, it could be made to persist at some higher pressure at the same temperature. By analogy with similar phenomena in solutions, this state was called supersaturated. The kinetic process leading to the collapse of supersaturated states is called nucleation.

A very essential feature of supersaturated states is their metastable character. It is a common experience that no such states persist for appreciable periods of time for vapors in contact with bulk liquid nor can they be created, in general, by cooling the walls of a containing vessel slowly since condensation occurs on the wall of the vessel.
If, however, one cools the vapor more rapidly than heat flow from the wall can occur, one can produce, momentarily, a supersaturated state. The rapid expansion of a vapor, for example, is approximately adiabatic with resultant cooling and this is the most common procedure for the production of such states. If the supersaturation is sufficiently great, condensation of the vapor results.

One characterizes the degree of supersaturation by the ratio of the actual pressure existing in the vapor to the equilibrium vapor pressure of bulk liquid at the same temperature. This ratio is known as the supersaturation ratio; the ratio just necessary for the onset of condensation is known as the critical supersaturation ratio.

Early workers in the field were led to the conclusion that the collapse of the supersaturated state could only be brought about through the action of a nucleus or seed, though the original concept of the nature of these nuclei was vague. In particular, the nuclei were not an inherent part of the system but were of some foreign origin. The study of these foreign nuclei, their nature and methods of production, occupies a major portion of the very early work and continues to play a vital role in modern investigations. Further investigation, however, revealed that the presence of foreign nuclei was sufficient to cause condensation but was not necessary. The two processes are distinguished by the terms foreign (or heterogeneous) and spontaneous (or homogeneous) nucleation, respectively.
Theoretical studies centered on the latter process and, in 1935, a formulation and solution of the problem was presented which was in excellent agreement with certain experimental results.

In the course of an investigation of the role of solid bodies as foreign nuclei for the nucleation of water vapor, it was found that the earlier experiments on the spontaneous nucleation of water vapor could not be reproduced. At about the same time, questions concerning the fundamental conceptual validity of the theoretical analysis were raised by Kirkwood and Buff, in criticizing the use of nucleation data as a test of certain theoretical developments concerning surface tension formulated by these authors.

Accordingly, an experimental study of the spontaneous nucleation of water vapor was undertaken and in the course of research, theoretical investigations were also performed.
II. PREVIOUS INVESTIGATIONS

1. Early Investigations

Aitken (1a) was apparently the first to observe the phenomenon of supersaturation in gases during the expansion of a saturated vapor. He concluded that the presence of dust particles or liquid droplets was necessary in order that condensation occur and noted that while filtration of the air materially reduced the number density of mist particles formed, the presence of combustion products had the opposite effect. As a result of a later investigation (1b) he concluded that the colors which appear in the light beam used to make the mist visible were influenced by the size of the mist droplets while the intensity of the scattered light was dependent upon the number density.

Closely paralleling Aitken's original work, Coulier (16), Kiessling (41), and R. von Helmholtz (77a) investigated the characteristics of the supersaturated state (by expansion of the saturated vapor) and similarly concluded that foreign nuclei were necessary for condensation to occur. The number of droplets formed was proportional to the number of foreign nuclei. Helmholtz investigated specific types of foreign nuclei and concluded that condensation was facilitated when the foreign nucleus reacted chemically with the vapor and, in fact, condensation occurred with almost no supersaturation. The degree of supersaturation required to form condensate varied with the size of the nuclei rather than their number.
Finally, he showed that electrification of the vapor increased the density of condensate (77b).

It was not until the classical researches of C.T.R. Wilson (82a), however, that the phenomenon of spontaneous nucleation was discovered and its distinction from heterogeneous nucleation clearly made. It was in the course of these investigations that the now famous Wilson cloud chamber was developed (82b). The essential features of the chamber are shown in Figure 1(a). The chamber (A) was a 15 cc. glass cylinder in which a closely fitting piston (P) moved, lubricated by the liquid of the vapor under investigation. The liquid also served to seal the upper chamber. The piston was elevated to some height by a head of air introduced at (C) (the gas and vapor in (A) being compressed) and the system was allowed to equilibrate. In time, the space above the piston became saturated with vapor. The air space beneath the piston was then connected by means of a rapidly opening valve (C) to the atmosphere. The pressure drop caused the piston to descend very rapidly, expanding the gas in the upper space in an essentially adiabatic fashion. The piston came to an abrupt halt when it hit the bottom of the chamber. The measurement consisted in varying the initial height of the piston (to vary the initial volume) and observing the effects of sequentially expanding the same volume of gas from decreasing initial volumes to a fixed final volume; the results were characterized in terms of the expansion ratio $r_e = V_2/V_1$. 
VARIOUS CLOUD CHAMBERS

FIGURE 1
though $P_1/P_2$ was measured. (Since, however, $V_2$ is always the same, $P_1/P_2 = V_2/V_1$). The results were also expressed in terms of the supersaturation ratio, $S$, which is computed using the adiabatic law to compute the final temperature and hence obtain the vapor pressure at $T_2$. *

Thus,

$$S = \frac{P_i \left( \frac{\gamma}{\gamma - 1} \right)^{\frac{\gamma - 1}{\gamma}}}{P_\infty} = \frac{P_i}{P_\infty} \left( \frac{T_2}{T_i} \right)^{1-\gamma} \tag{2.1}$$

where

$$T_2 = T_i \left( \frac{T_i}{T_\infty} \right)^{1-\gamma} \tag{2.2}$$

and

$$\gamma = \frac{C_p}{C_v}$$

and $p_i$ = initial vapor pressure in the chamber

$p_\infty$ = equilibrium vapor pressure at the final temperature $T_2$

The primary advantage over earlier expansion chambers, used by Aitkens and others in such studies, was the rapidity of the expansion which should have been more nearly adiabatic. The speed was increased by working with a very small chamber.

The investigation of water vapor showed that, initially, very slight expansions produced a dense fog but, in time, for the same sample of gas an expansion ratio of $r_e = 1.02$ would not produce any condensate and one had to have $r_e = 1.25$ **

---

* The results are sometimes reported in terms of the "critical" expansion ratio, $r_e \text{ (critical)}$, which is easily converted to $S \text{ (critical)}$, the critical supersaturation ratio.

** This would be a critical expansion ratio.
to obtain condensation. The initial expansions were interpreted as "cleaning" expansions causing dust nuclei to be rained out.

It was further found that in the range $1.38 > r_e > 1.252$ the appearance of the condensate was "rainlike" with relatively few but large droplets. The number density was essentially constant in this range, unaffected by sunlight or filtration of the air. When the ratio, $r_e$, exceeded $1.38$ a sharp increase in number density (and corresponding decrease in droplet size) was noted. Colors were observed when the mist was viewed at some angle to the light beam.* The results are summarized in Table 1.

Wilson interpreted these results as follows:

1. A small number of nuclei ($<100$ per cc.) effective in the range $1.38 > r_e > 1.252$ exist whose concentration is dependent upon the carrier gas (they do not occur in freshly prepared $H_2$).

2. When $r_e > 1.38$, the number of nuclei rapidly increases until the number density is in the millions per cc. These nuclei were thought to be aggregates of water molecules to account for their huge numbers; hence the term spontaneous nucleation.

* These results were also obtained in preliminary experiments with a larger chamber.
## TABLE 1
Data of Wilson for Water

<table>
<thead>
<tr>
<th>Gas</th>
<th>Rain to C</th>
<th>$(P_1/P_2)_{crit}$</th>
<th>Cloud to C</th>
<th>$(P_1/P_2)_{crit}$</th>
<th>Comment</th>
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</thead>
<tbody>
<tr>
<td>Air</td>
<td>18.5</td>
<td>1.247</td>
<td>17.5</td>
<td>1.373</td>
<td>Rain</td>
</tr>
<tr>
<td></td>
<td>17.5</td>
<td>1.261</td>
<td></td>
<td>1.378</td>
<td>Fog</td>
</tr>
<tr>
<td></td>
<td>15.5</td>
<td>1.254</td>
<td></td>
<td>1.375</td>
<td>Rain</td>
</tr>
<tr>
<td></td>
<td>16.5</td>
<td>1.251</td>
<td></td>
<td>1.378</td>
<td>Fog</td>
</tr>
<tr>
<td></td>
<td>18.5</td>
<td>1.260 ± .004</td>
<td>15.0</td>
<td>1.372</td>
<td>Rain</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.378</td>
<td>Fog</td>
</tr>
<tr>
<td>$O_2$</td>
<td>17-21</td>
<td>1.257</td>
<td>18-21.5</td>
<td>1.383</td>
<td></td>
</tr>
<tr>
<td>$CO_2$</td>
<td>17-19</td>
<td>1.36-1.37</td>
<td>17.5</td>
<td>1.535</td>
<td>$CO_2$ solubility in water complicated the measurements.</td>
</tr>
<tr>
<td>$H_2$</td>
<td>No rainlike condensation for freshly prepared $H_2$.</td>
<td>20.5-22</td>
<td>1.380</td>
<td></td>
<td></td>
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<td>$Cl_2$</td>
<td>20-21.5</td>
<td>1.30</td>
<td>18</td>
<td>1.45</td>
<td>$Cl_2$ solubility in water introduced complications. The rain density was higher than for other gases.</td>
</tr>
<tr>
<td>$N_2$</td>
<td>11-17.5</td>
<td>1.262</td>
<td>13-15</td>
<td>1.38</td>
<td></td>
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</table>

$(P_1/P_2)_{crit}$ Colors Visible in Scattered Light

| Air   | 1.41-1.42 | Brilliant greens and blue greens |
|       | >1.42     | Rapid change from blue to red and violet |
|       | 1.44      | Red to yellow |
|       |           | White with blue tinge |
One interesting point was noted by Wilson. Whenever condensate was formed, the very next slight expansion yielded "rain" and preliminary cleaning expansions were required before the chamber could be used again. The nuclei so formed are referred to as re-evaporation nuclei.

In the same investigation, the influence on the condensation process of various types of radiation and the presence of various metals in the chamber was studied. Wilson's summary is essentially reproduced here. (82c).

1. X-rays produce nuclei effective at \( r_e = 1.25 \). Their number density is a function of the beam intensity. Uranium compounds produce similar effects.

2. Weak ultraviolet radiation on water saturated \( O_2 \) yields nuclei effective at \( r_e = 1.25 \); strong ultraviolet radiation apparently causes the nuclei to grow since the critical expansion ratio depends upon the intensity and duration of the exposure. Very strong ultraviolet light will cause growth to visible droplets in an unsaturated atmosphere without expansion. Wilson considered these nuclei to be a product of some photochemical reaction (presumably \( H_2O_2 \)).

3. The presence of an amalgamated Zn plate causes a dense fog at a value of \( r_e \) at which, in the absence of the metal, a few drops would be produced. Clean Zn, Pb show a much weaker effect; Cu and Sn are without effect.
Wilson identified some of the nuclei effective in the range $1.38 > r_e > 1.25$ as ions by carrying out experiments in which an electric field was applied to the region of observation in the chamber. Neither the nuclei produced by ultraviolet light nor those from metals were affected by a field of 150v/cm; the X-ray nuclei were affected. Consequently, it was thought that ions were not the only nuclei effective in this range. The cloud limit was not affected by a field strength of 225v/cm.

Wilson (82d), in further investigations with ions, discovered that positive and negative ions behave differently in the condensation process. In particular, for water, negative ions were preferred nuclei, being effective at $r_e = 1.25$ while positive ions did not become effective until $r_e = 1.31$. Experiments were also described which showed that in naturally ionized air, a field of 400 v/cm did not affect the number density of condensate in the range $r_e = 1.25$ to 1.38. In order to permit the identification of these unknown nuclei, which are unaffected by a preliminary clearing field but cause condensation at exactly the same expansion ratio as artificially produced ions, he postulated the production of ions by the expansion.

In the years that followed, many other investigators repeated and extended these researches on foreign nuclei. Before proceeding to a detailed survey of the experimental investigations of spontaneous nucleation, the major findings on heterogeneous nucleation will be briefly reviewed to point out the varied nature of the possible influences upon
the condensation process.

2. Heterogeneous Nucleation

Barus (6a,b) carried out extensive studies on condensation nuclei utilizing the colors visible in the scattered light from the cloud to estimate the size and number density of the droplets. He concluded that large nuclei could be filtered out, but that smaller nuclei (identified with Wilson's reevaporation nuclei) could not.

The influence of ozone on the condensation process was studied by a number of investigators. Leithauser and Pohl (48) concluded that due to chemical reaction between \( \text{O}_3 \) and \( \text{N}_2 \) to yield acid anhydrides, condensation of water was promoted. (Pringl (61) reported similar observations). Cooling the gas to -79°C removed the nuclei, presumably due to condensation of the nitrogen oxides. Other acid anhydrides also promoted condensation.

Bieber (8) reported (blue) cloud formation in the presence of \( \text{O}_3 \) *without* \( \text{N}_2 \) being present. He concluded that \( \text{H}_2\text{O}_2 \) was the responsible nucleus in accord with Wilson's earlier idea.

Investigations by Sachs (67) of nuclei produced by ultraviolet radiation indicated that they were uncharged,

* From an AC field, ultraviolet radiation, or direct introduction of \( \text{O}_3 \).
stable (persisting for over an hour) and not removable by
cooling. Heating to 180°C, however, destroyed them. All
gases investigated (air, CO₂, O₂, N₂, CHCl₃) except H₂ gave
similar results. The number of nuclei produced in H₂ was
very small.
Saltmarsh (68) reported that nuclei were not formed
under the influence of ultraviolet light in the absence of
O₂ or CO₂.
Recently, Farley (19) confirmed that these nuclei are
electrically neutral and noted that a deuteron beam produced
similar nuclei. McHenry and Twomey (52) found nuclei pro-
duction at wavelengths in the range 2345-2399Å (an absorp-
tion band of O₂) in air, N₂, and O₂. They believed that in
moist air, NH₃ was formed as the main nucleus. A report by
Gutzwiller and Verzar (30), however, indicates that NH₃ is
ineffective in filtered air.
An interesting observation by Owen (57) was that the
sudden cooling of dry "dust-free" air to liquid air temp-
eratures produced nuclei of some sort. Gendron(26) reported
a similar observation.
The huge number of investigations of nucleation on ions
has been summarized by Volmer (76a) and Needles(55) and the
previous work shows simply that various substances may show
preferential condensation on positive or negative ions, or
neither.
For condensation of mixed vapors (very much used in
nuclear physics research) the critical supersaturation ratio is always decreased relative to that of pure vapor (76f).

The information to be gleaned from this summary is simply that foreign nuclei of any sort, derived in any manner, tend to cause condensation at lower supersaturations than would exist of they were absent. An immediate experimental problem is indicated; the removal of all foreign nuclei must somehow be guaranteed in order to carry out spontaneous nucleation studies.

3. Spontaneous Nucleation

The first highly detailed investigation of spontaneous nucleation, after Wilson, was carried out by Andren (4) who measured the number concentration of droplets formed as a function of the terminal supersaturation ratio. The form of the apparatus is shown in Figure 1(b). The chamber volume A was either "small" (60 cc) or "large" (260cc). The piston P was supported by air pressure. Connection of the system to a vacuum reservoir (through C) caused the piston to descend and the gas in A to be expanded.

The measurements were made for rainlike condensation by directly observing the number of droplets formed in a given volume. For very dense clouds, the average particle size was computed from the fall velocity and Stoke's law. Together with a knowledge of the total vapor pressure and volume one could make a rough estimate of the number concentration assuming all droplets were the same size. An electric field could be applied to the volume A.
The initial experiment on water vapor used filtered air, cleaned by repeated expansions. The results essentially confirm those of Wilson, though Andren notes that the "limits" of 1.25 and 1.38 set by Wilson are not sharp and the definition of fog is not clear.

To test for the possibility of impurity, the experiment was repeated except that the air was passed through a cold spiral (~79°C), over CaCl₂, P₂O₅, and filtered before entering the chamber. The chamber itself was heated until steam issued freely from the exit port (R). The results were unchanged.

In Figure 2 the data of Andren on condensation of water in air and H₂ are graphically summarized.

For water condensing in naturally ionized air, the sharp rise in number density in the region of the Wilson cloud limit (S~7) is noted when an external clearing field of 330V/cm is applied (Curve Ic). When a smaller field is applied (Ib), the sharp rise occurs at a lower supersaturation. Finally, for condensation on ions (without a field), the break appears in the region of the rain limit of Wilson (Ia).

It is interesting to note that the difference in the number of droplets formed at the cloud limit in the experiments with and without a field (Ia, Ic) is of the order of the number per cc of ion pairs in naturally ionized air (~1000) (76g).

The influence of artificial ionization (Curves II, III) is striking. For the ionized gas, the more active the source (Radium) the lower the supersaturation at which condensation
FIGURE 2
DATA OF ANDREN

I Naturally Ionized
II 0.05 mg. Ra
III 2.5 mg. Ra

a No field
b 1.2 volts per cm.
c 275-330 v. per cm.
becomes appreciable. Much more striking is the lowering of the apparent critical supersaturation ratio \( \Pi_{ic} \) compared to the corresponding case for naturally ionized air \( \Pi_c \). This implies that not all the ions formed are removed by the electric field.

The results using \( H_2 \) confirm Wilson's finding that no rainlike condensation occurs but more striking is the dependence of the apparent critical supersaturation ratio on the size of the chamber \( (I_{a-s}, I_{a-l}) \). Andren considered the possibility that the heat conductivity of \( H_2 \) was responsible for the necessity of a greater expansion in the smaller chamber to effect condensation but observation of the process in the region of the walls showed no particular deviation in number density.

Powell (60) investigated the effect on the condensation process of varying the total pressure in the chamber (keeping the vapor pressure constant). The chamber was an exact duplicate of that used by Wilson (Figure 1a). The criterion of "cloud" was taken as the appearance of a mauve tint in the light scattered from condensate (see Table 1).

Typical results for water vapor are shown in Figure 3a. The sharp dependence of the nominal critical supersaturation ratio (calculated from the initial conditions and \( (r_e)_{critical} \)) upon the ratio of vapor pressure to total pressure is clearly indicated. (Experimentally, the critical supersaturation ratio was found to depend upon the rate of expansion when the
Figure 3
total pressure was low). The error in $S$, based on Powell's estimated $\frac{1}{2}$% error in $r_e$ and $0.1^\circ C$ error in $T_1$, is approximately 5% (see Chapter III, section 8).

Powell explained the results at low total pressures as due to an enrichment of the vapor phase of the cooling gas by diffusion from the warmer liquid on the walls (and on the piston).* The liquid water is not cooled by the expansion and, hence, as the carrier gas and vapor cool, a vapor pressure gradient is set up. The rate of evaporation depends upon the total pressure though its effectiveness in altering $S_{\text{critical}}$ depends upon the cooling rate (or rate of expansion). For high pressures and high speed expansions, the result is negligible. (In Wilson's experiments, the ratio of the vapor pressure to total pressure was about .01).

Powell pointed out for the first time the second vital role played by the carrier gas in these experiments. It not only provides the thermal reservoir for cooling the vapor but also suppresses the diffusion of vapor from the hot liquid wall to the vapor in the carrier gas.

If one extrapolates the results to $R_f \to \infty$ or $\frac{V_2}{V_1} \to 0$ limiting rain and cloud limits can be obtained (Table 2).

The high temperature values quoted by Powell ($>30^\circ C$) are calculated on the basis of an extrapolative procedure

* The increase in $\frac{V_2}{V_1}_{\text{critical}}$ is then clearly due to the much greater mass of vapor that must be cooled.
and are probably not precise.

**TABLE 2**

<table>
<thead>
<tr>
<th></th>
<th>T₁</th>
<th>V₂/V₁</th>
<th>T₂</th>
<th>S_{critical}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloud</td>
<td>18°C</td>
<td>1.370</td>
<td>-16.4°C</td>
<td>7.80</td>
</tr>
<tr>
<td></td>
<td>7°C</td>
<td>1.375</td>
<td>-26.4°C</td>
<td>8.95</td>
</tr>
<tr>
<td>Rain</td>
<td>18°C</td>
<td>1.245</td>
<td>-6.5°C</td>
<td>3.98</td>
</tr>
<tr>
<td>(or Ion)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Powell also noted the existence of reevaporation nuclei.

Anderson and Froemke (3a) redesigned the expansion apparatus in such a manner as to prevent the liquid from being splashed about by the motion of the piston and yet maintain a very rapid expansion (Figure 1c). Its operation is quite similar to that of Andren's chamber. These authors felt that previous workers did not obtain a truly adiabatic expansion. They obtained a value of the critical expansion ratio for the ion (or rain) limit of

$$ (r_e)_{\text{critical}} = 1.2006 \pm 0.0001 $$

Therefore $S = 3.0$  
$T_1 = 298.1$  
$T_2 = 277.1$

and in a later investigation (3b) found the value at the cloud limit to be

$$ (r_e)_{\text{critical}} = 1.339 \pm 0.001 $$

and hence $S = 6.65$  
$T_1 = 298.1$  
$T_2 = 265.3$

These results are distinctly lower than those reported previously.

In 1934, Volmer and Flood (76n) carried out a pains-taking investigation of the spontaneous nucleation of various
vapors. The apparatus is shown in Figure 1(d). The experiment was similar to all others in that successively larger expansions were carried out until condensation occurred (after preliminary cleaning expansions). According to the authors, droplet formation set in sharply and reproducibly though splashing of the liquid did cause observational difficulties.

The criterion of condensation used was that a small increase in $r_e$ yielded a definite increase in the number of droplets/cc.

The validity of the assumption of an adiabatic process was checked for this chamber by carrying out expansions with a resistance thermometer in the chamber.* The minimum temperature reached was in agreement with that predicted theoretically and persisted for a measurable time. When $r_e$ exceeded 1.4, however, the lowest temperature reached deviated from that expected ideally. The upper limit of 1.4 would probably be raised for larger chambers (76 l)

The results for water and various organic compounds are given in Tables 3 and 4 along with the results of some earlier investigators for the organic liquids.

The authors claim a precision of ±.1 cm in $(P_1/P_2)$ (out of 15 cm) without a field and ±.1 to .2 with the field. This

* There was no condensable vapor in the chamber (76k).
### TABLE 3

Data of Volmer and Flood for Water

<table>
<thead>
<tr>
<th>$T_1$</th>
<th>$(r_e)_{\text{crit}}$</th>
<th>$T_2$</th>
<th>$S_{\text{crit}}$</th>
<th>$S_{\text{calc}}(\text{B.D.Z.})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.0</td>
<td>1.269</td>
<td>275.3</td>
<td>4.22</td>
<td>4.16</td>
</tr>
<tr>
<td>302.8</td>
<td>1.268</td>
<td>275.2</td>
<td>4.21</td>
<td></td>
</tr>
<tr>
<td>300.9</td>
<td>1.258</td>
<td>274.3</td>
<td>4.06</td>
<td></td>
</tr>
<tr>
<td>301.7</td>
<td>1.267</td>
<td>274.3</td>
<td>4.21</td>
<td></td>
</tr>
<tr>
<td>288.3</td>
<td>1.275</td>
<td>261.4</td>
<td>4.91</td>
<td>4.96</td>
</tr>
<tr>
<td>288.2</td>
<td>1.279</td>
<td>261.0</td>
<td>5.04</td>
<td></td>
</tr>
<tr>
<td>288.1</td>
<td>1.278</td>
<td>261.0</td>
<td>5.02</td>
<td></td>
</tr>
<tr>
<td>287.1</td>
<td>1.273</td>
<td>260.5</td>
<td>4.89</td>
<td></td>
</tr>
<tr>
<td>287.5</td>
<td>1.278</td>
<td>260.4</td>
<td>5.06</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 4

Critical Expansion Ratios and Supersaturations

<table>
<thead>
<tr>
<th>Substance</th>
<th>( T_1 )</th>
<th>( (r_e)_{\text{crit}} )</th>
<th>( T_2 )</th>
<th>( s_{\text{crit}} )</th>
<th>( S_{\text{calc}} )</th>
<th>( (r_e)_{\text{crit}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>295</td>
<td>1.285</td>
<td>270</td>
<td>3.20 ( \pm ) 1</td>
<td>1.8</td>
<td>(a) 1.42, 1.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(b) 1.378, 1.306</td>
<td>1.251</td>
</tr>
<tr>
<td>Ethanol</td>
<td>289.5</td>
<td>1.172</td>
<td>277.2</td>
<td>2.34 ( \pm ) 0.05</td>
<td>2.28</td>
<td>(a) 1.25, 1.20</td>
</tr>
<tr>
<td>n-propanol</td>
<td>289</td>
<td>1.190</td>
<td>270.4</td>
<td>3.05 ( \pm ) 0.05</td>
<td>3.22</td>
<td>(b) 1.237, 1.201</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.178</td>
<td></td>
</tr>
<tr>
<td>i-propanol</td>
<td>283.2</td>
<td>1.190</td>
<td>264.7</td>
<td>2.80 ( \pm ) 0.07</td>
<td>2.89</td>
<td></td>
</tr>
<tr>
<td>n-butanol</td>
<td>291</td>
<td>1.206</td>
<td>270.2</td>
<td>4.60 ( \pm ) 1.3</td>
<td>4.53</td>
<td></td>
</tr>
<tr>
<td>Nitromethane</td>
<td>291.5</td>
<td>1.462</td>
<td>252.2</td>
<td>6.05 ( \pm ) 1.3</td>
<td>6.22</td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>290</td>
<td>1.175</td>
<td>240</td>
<td>12.3</td>
<td>10.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.670</td>
<td>8.6</td>
<td>(c) 1.486</td>
<td></td>
</tr>
</tbody>
</table>

* Data of Volmer and Flood
(a) Donnan, Phil. Mag. [6] 3 · 305 (1902)
(b) Prizbrom, Ber. Akad. Wiss. Wien IIa 118 331 (1909)
(c) Laby, Phil. Trans. Roy. Soc. A208 445 (1908)

\( \Theta \Theta \) refer to positive or negative ion nuclei.
leads to an error of about 5% in $S_{\text{critical}}$. Volmer notes that the small region behind the upper electrode is field-free and so some ions would not be removed from the chamber. He regards this as insignificant.

For water condensing in naturally ionized air ($\sim 10^3$ ions/cc), the critical supersaturation ratio found is in essential agreement with earlier work:

$$S_{\text{critical}} = 4.1 \text{ at } 265^\circ \text{K} \quad (r_e)_{\text{critical}} = 1.252)$$

The ratios for spontaneous nucleation are distinctly lower than previously reported. The difference was due to the different criterion of condensation employed. Volmer felt that the Wilson criterion (cloud) was not correct.

Loeb, Kip, and Einarsson (50) used a chamber similar to that used by Wilson in an investigation of the preferential condensation of $\text{H}_2\text{O}$ on positive or negative ions. (Figure 1(e)). Their results are again quite different for spontaneous nucleation (Table 5) though they agree with Wilson's results for ion condensation. The criterion of condensation was observation of a "definite cloud", not "4 or 5 drops".

**TABLE 5**

<table>
<thead>
<tr>
<th></th>
<th>Spontaneous</th>
<th>Positive Ion</th>
<th>Negative Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>1.32</td>
<td>1.31</td>
<td>1.25</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{OH}$</td>
<td>1.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH}$</td>
<td>1.33</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In 1941, Frey (23) reported an investigation of the dependence of the number of droplets formed as a function of supersaturation ratio. (The apparatus is shown is Figure 1(e)). He obtained as the limiting values of S for the onset of condensation just the results of Volmer and Flood (Figure 3b). These were obtained by an extrapolative procedure (since the minimum number of droplets that could be detected was $10^3$/cc) and represent a maximum for $S_{\text{critical}}$. The purification scheme was quite unusual. The author attempted the removal of impurities by ionizing the gas in the chamber with an X-ray discharge (for 10 seconds) and then, 5 seconds later, carrying out the expansion. The field was on at all times ($\sim 150$ V/cm). From Andren's data, however, the difficulty of removing nuclei produced by artificial ionization is clearly indicated.

The effect of sequential expansion of the same gas sample after ionization is shown in Figure 3b. The dotted curve (a) is the same as in the first figure.

The first departure from the usual experimental procedure was due to Sander and Damköhler (69). The apparatus (Figure 1(g)) consists simply of a 0.7 liter flask connected to a 12 liter vacuum reservoir. The expansion is initiated by opening the 20mm bore stopcock connecting the flask and reservoir; no piston is used. Since the volume of air is not enclosed, the air has to be purified. The authors used a system consisting of filters and freezing traps, then saturated the air in some manner and passed it into the
chamber (Figure 4). The purification scheme was varied with no change in results. The saturation scheme was similarly altered, again without effect.

The results were expressed in the form of equations:

\[ S_{\text{critical}} = \frac{780}{T} - 1.521 \text{ (no ions)} \text{ for } T > -62^\circ C \]
\[ S_{\text{critical}} = \frac{765}{T} - 1.537 \text{ (ions)} \]

Thus, at 260°K, \( S_{\text{critical}} = 4.32 \text{ (no ions)} \) and 4.08 (with ions).

The results for spontaneous nucleation are the lowest reported in all the investigations but, again, the ion limit is in agreement with earlier work.

From this brief survey, it is clear that no agreement exists as to the point at which spontaneous nucleation occurs. There appears to be no question concerning the ion limit.

During the course of this research, Pollerman (58) and Pound (59) reported spontaneous nucleation experiments which apparently supported the Volmer-Flood results. A close examination of Pound's reported results show this not to be so. Discussion of their work will be deferred until our own results have been presented. From this research and some very recent data of Pound, the conclusion seems to be that the higher supersaturation, reported by Wilson, is more nearly correct.

4. The Theory of Nucleation

The theory of the nucleation process was initiated with the proof by Kelvin (40) that the vapor pressure over a curved liquid surface is higher than over a plane surface at
Methoqs of operation

<table>
<thead>
<tr>
<th>Partial flow</th>
<th>Partial flow</th>
<th>Position of the shop cocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>line I</td>
<td>line II</td>
<td>5</td>
</tr>
<tr>
<td>A</td>
<td>Bacteria filter</td>
<td>Not used</td>
</tr>
<tr>
<td>B</td>
<td>100 cm absorbent cotton</td>
<td>&quot;</td>
</tr>
<tr>
<td>C</td>
<td>Bacteria filter</td>
<td>100 cm absorbent cotton</td>
</tr>
<tr>
<td>D</td>
<td>100 cm absorbent cotton</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Purification Line - Sander & Damköhler

Figure 4
the same temperature. He derived the relation, for a spherical interface,

\[ P_2 = P_1 + \frac{2\sigma}{r} \]  \hspace{1cm} (2.3)

where \( P_2 \) is the pressure on the concave side of the surface, \( P_1 \) is the pressure on the convex side and \( \sigma \) is the surface tension. Applied to a small droplet, it shows that the pressure inside the drop, \( P_2 \), is greater than the pressure outside, \( P_1 \), by \( \frac{2\sigma}{r} \) and thus small droplets can coexist with a vapor which is supersaturated with respect to a bulk phase.

The brilliant work of Gibbs marks the first real contribution to the theory. An examination of the condition for the formation of a new phase from one which had previously existed was carried out! To do this in a rigorous fashion, Gibbs developed an exact thermodynamic treatment of surfaces (27a) and was able to show that the Kelvin law, under certain conditions, represents the condition of thermodynamic equilibrium between phases separated by a curved interface (27b). He showed that in order to convert a vapor phase, initially homogeneous, to a new liquid phase, work would have to be done on the original phase in the amount \( \sigma A/3 \) where \( \sigma \) was interpreted as the macroscopic surface tension and \( A \) the area of the curved interface formed (27c).

When this formalism is applied to observed degrees of supersaturation, the radius of the droplet involved is found to be of the order of \( 10^{-7} \) cm., the droplets consisting of 50 to 100 molecules. This extremely small droplet is not visible; the observed droplets are assumed to arise from these
submicroscopic entities by some growth process.* The theories of nucleation utilize a thermodynamic development which applies to minute droplets and questions of growth to visible droplets do not arise. The theories relate to the conditions under which the spontaneous conversion of a homogeneous phase into two phases will occur.

The quantity $\sigma A/3$ is positive, and hence spontaneous conversion should not occur \( (27d) \). Volmer and Weber \( (76m) \), however, considered the process of nucleation to be essentially a fluctuation phenomenon (since the average properties of the system are not significant with respect to its stability \( (76b) \)) and applied the fluctuation theory of Einstein \( (73b) \). One computes the relative probability, $p_1$, of a given state being reached by fluctuation from some initial state, from the reversible work, $\Delta \Phi$, necessary to transform the system from the initial state to the new state.

The explicit formulation yields
\[
p_1 = \text{constant exp} \left( -\frac{\Delta \Phi}{kT} \right) \tag{2.4}
\]
Gibbs computed the work of formation of a droplet from an initially homogeneous vapor and, hence, the probability of this event is proportional to $\exp \left( -\frac{\sigma A}{3kT} \right)$.

On this basis, Volmer and Weber arrived at an expression for the rate of formation of such droplets as could remain in

---

* The submicroscopic droplets are identified with Wilson's spontaneous nuclei.
equilibrium with a vapor whose pressure was higher than the equilibrium vapor pressure at the same temperature (a super-saturated vapor). These droplets are called (critical) nuclei inasmuch as will be shown below*, (critical) nuclei are capable of spontaneous growth. Thus,

\[ I = B \exp \left( -\frac{\sigma A}{3kT} \right) \]  \hspace{1cm} (2.5)

\( I \) = rate of formation of critical nuclei per unit volume per unit time

\( B \) = an unknown constant

Farkas (18) extended the treatment, evaluated a portion of \( B \), to obtain

\[ I = C \frac{p_2}{A} \exp \left( -\frac{\sigma A}{3kT} \right) \] \hspace{1cm} (2.6)

where \( p_2 \) is the vapor pressure of the droplet, \( A \) its area.

There still remained the unknown constant \( C \).

In 1934, Becker and Döring (7a) rejected the fluctuation approach and derived, on a kinetic basis, an expression for \( I \) in which no undetermined constants appeared. The treatment took account of both the growth of molecular aggregates (or droplets) by collision and their decay by evaporation, these detailed processes having no place in the fluctuation theory.

They found for the rate of nuclei production per unit volume, \( Idt \),

\[ Idt = \frac{\sqrt{2} \pi^{3/2} (p_\infty)^2 \sqrt{\sigma} M}{\sqrt{\pi} R^2 T^2 P} \left( \frac{P}{P_\infty} \right)^2 \exp \left[ -\frac{16 \pi \sigma^2}{3kR^2 P^2 T^2 (\ln p_\infty)} \right] \] \hspace{1cm} (2.7)

* See Chapter IV.
where \( \Delta = \text{condensation coefficient (assumed 1)} \)
\[ \rho = \text{density of the liquid} \]
\[ m = \text{molecular weight per molecule} \]

the quantity in the exponent being \( \sigma A/3kT \) expressed in a different form (27h).

The results calculated on the assumption that the proper value of \( Idt \), corresponding to the observed condensation, was unity agreed with the data of Volmer and Flood to within a few percent. (See Tables 3, 4). The discrepancies for methanol and ethyl acetate were attributed to experimental error due to the high partial pressure of methanol (14%) in the expansion chamber and the non-adiabaticity of the expansions used in the measurements on ethyl acetate (76c).

The problem would seem to have been closed except for minor refinements in the mathematical technique of the solution. Frenkel (22a) introduced the concept of heterophase fluctuations, in which a distribution of molecular aggregates (of liquid density) of varying sizes exists at all times in the vapor, and generated this distribution. Zeldowitch (84b) transformed the relevant difference equation set up by Becker and Döring to a partial differential equation and, in the solution, utilized the Frenkel distribution. The result of the calculations agreed closely with the more complicated analysis of Becker and Döring (5).

Further "corrected analyses" were given by Volmer (76a) and Sander and Damköhler (69) but the results were essentially unaltered.

It was concluded that the earlier experiments eg. Wilson
were in error and that the Volmer-Flood data represented the true experimental situation. The one apparent discrepancy, the failure of the nucleation frequency* to agree with the results of Andren on the number of droplets formed in this range of supersaturation was taken not to be meaningful for these investigations due to other complicating experimental factors.

5. Statement of the Problem

In 1949, Kirkwood and Buff (42a) and Tolman (73a) indicated that the surface tension of a fluid should depend upon its curvature, $c$, and in particular, it should decrease with increasing curvature (or decreasing radius, since $r = 1/c$). LaMer and Pound (45) reasoned that since the calculation of the nucleation rate depends strongly on the surface tension, varying as $\exp[-\sigma^3]$, and the $\sigma$ involved really refers to a submicroscopic drop with a highly curved surface, a more correct value of $\sigma$ would be given by Tolman's formula (for computing facility). They calculated the critical supersaturation ratio with the revised value of $\sigma$ and, naturally, this did not yield the experimentally observed values of Volmer and Flood. Pound and LaMer concluded that these theories of surface tension were incorrect. Kirkwood and Buff (42b) promptly replied that the application of macro-thermodynamic concepts to such small droplets as arise in the nucleation

* The number of nuclei formed per cc. per second.
theory is very questionable and even questioned the validity of the experimental results. They indicated explicitly certain theoretical difficulties (even allowing the use of macro concepts) which could be significant.

It appeared, however, that the theory of Becker and Döring, though resting upon a very shaky conceptual foundation, could indeed predict with remarkable precision the experimental results.

In the course of investigations on condensation phenomena in wind tunnels Head (44) reported that the use of the Becker-Döring-Zeldowitch* theory, for predicting the location of shocks due to the condensation of the components of air, did not lead to the observed results although similar calculations by Oswatich (56) for water condensation shocks in hypersonic wind tunnels yielded quite good agreement with experiment. Other investigators (17, 47, 78) reported similar discrepancies even with water vapor.

Serious doubts as to the validity of the quantitative B.D.Z. theory were raised and the experimental data which validated the theory, based upon cloud chamber studies, was not indisputable. Accordingly, an intensive experimental investigation of the spontaneous nucleation of supercooled water was undertaken, together with theoretical investigations, the latter initiated in an attempt to account for certain experimental discrepancies. Several investigations of the theory appeared

* Hereinafter referred to as the B.D.Z. theory.
in the literature during the course of this research but discussion of them will be reserved for the appropriate place in the detailed presentation.
1. Basic Concepts of the Measurement

It is important at the outset to understand just what assumptions enter into the comparison between theory and experiment for the type of experiment under consideration, the relatively slow cloud chamber expansion.

Briefly, the carrier gas, saturated with the vapor, is caused to undergo a cooling process by means of an adiabatic expansion and when the cooling is sufficiently large the appearance of condensate, suspended in the vapor, is noted.*

The significant experimental parameters are the pressure and temperature at the point of condensation. One does not measure the actual rate of condensation: this is instantaneous to an observer. Since the R.D.Z. theory predicts a very sharp rise in rate as the supersaturation increases, one assumes that the instantaneous nature of the observed transition is an experimental reflection of this aspect of the theory.

This immediately raises the question as to what rate of nuclei production corresponds to the observed number density of droplets. There are really two points to be considered: how fast do the nuclei grow to visible size and, simultaneously, does the process yield nucleation only once or continuously, while the initial nuclei are growing (the latter being

*A carrier gas is required to be able to expand the vapor and gas sufficiently to obtain any appreciable cooling.
determined by the rate of growth of nuclei and the rate of cooling of the vapor)?

The usual assumption is to consider the appearance of 1 drop/cc to be equivalent to the numerical equivalent of the isothermal, isobaric rate of nuclei production at the terminal conditions integrated over the time of the process (76d). The growth is assumed to be nearly instantaneous so that the vapor concentration is reduced too rapidly to permit further nucleation once the initial nucleation has occurred. The validity of the growth assumption is difficult to assess. The use of the criterion of 1/cc may be questioned from a practical point of view, even assuming the 1:1 correspondence between the nuclei produced and the droplets observed, since an impurity concentration of this magnitude is not unreasonably high. (This point will be considered later).

Summing up, the experimental measurement of the point at which condensation occurs is related to a calculated rate process of nucleation by means of an unknown coupling of subsequent growth of the nuclei to a visible size. The usual assumption ignores the growth process but it should be noted that in wind tunnel expansions, this cannot be valid and is not ignored (56). The growth calculations are necessarily crude. The theoretical criterion of condensation is also fundamentally quite different and relates to the conditions for shock formation (see Chapter V).

2. Operating Characteristics of Cloud Chambers

Before proceeding to an examination of earlier experi-
mental techniques and the details of the experimental research undertaken here, it will be profitable to briefly examine the characteristic features of the operation of a cloud chamber.

Basically, the process consists in the self-cooling, by their expansion, of the vapor and carrier gas while the container remains at the initial temperature. It is apparent that failure to cool the walls of the vessel immediately makes available to the gas a large source of heat as it is cooling. Successful operation, in the sense of obtaining a well-defined process (an adiabatic expansion), depends upon completing the cooling process before the conduction of heat from the walls can exert any significant influence. The rapidity of expansion and size of the chamber will obviously determine how well one can satisfy this requirement. That it is possible at all is due to the possibility of a much greater rate of cooling of the vapor and gas compared to the rate of heat conduction to the gas.

Two types of chamber are in use, the volume-defined and the pressure-defined, the terminology referring to the method of producing the desired expansion. Their characteristics have been examined in detail by Wilson (83a) and we shall essentially summarize his analysis.

The volume-defined chamber is operated so that the expansion is determined by a mechanically fixed increase of the volume. The process is then characterized by the expansion ratio (which is directly measurable) and, if adiabatic, the
final temperature, $T_2$, is given by Equation 2.2.

It must be realized that one cannot really calculate the supersaturation at the condensation point since there is no longer any supersaturation once condensation has occurred. If the relations are assumed to be valid up to the point just prior to condensation, while the phase is still homogeneous on a macro scale, a supersaturation varying very slightly from the correct one may be calculated. This is not a severe approximation. The supersaturation at any point is then given by Equation 2.1 and the critical supersaturation is obtained from the critical expansion ratio.

It is interesting to follow the temporal development of the supersaturation in a volume-defined chamber. This is shown in Figure 5a. The rate at which supersaturation is produced accelerates from the initial time $t_1$ until the process comes to an abrupt halt at $t_2$. Shock phenomena set in at this point.

The effect on the adiabaticity of expansion in volume-defined chambers, due to heating by the wall, has been studied by Williams (81). If one defines the persistence of the supersaturated state as the time, $\tau$, required for the gas in the chamber, expanded to $r_e = 1 + r + \delta r$, to alter its condition (by warming up) to such an extent that its state was equivalent to that which would be reached were the expansion ratio only $r_e = 1 + r$, then the author's calculation yields,

$$\tau = .77 \frac{P C_p}{(1-1)^2} \left( \frac{V}{S} \right)^2 \left( \frac{\delta r}{r} \right)^2$$

(3.1)
TEMPORAL DEVELOPMENT OF SUPER SATURATION

FIGURE 5
where \( \rho \) = Gas density  
\( c \) = Gas specific heat  
\( \chi \) = Gas thermal conductivity  
\( v \) = volume of chamber  
\( s \) = surface area of chamber

For large chambers, this time is long indicating a negligible heating effect. The importance of the persistence of the supersaturated state is simply that it creates a condition under which the nuclei can grow in the supersaturated vapor. If growth is really instantaneous, this is not important, but instantaneous growth is not likely and the allowable time of growth should be important.

The pressure-defined chambers operate on the principle of equalizing the pressure between two vessels to halt the expansion. The analysis, as given by Herzog (37), is more complicated and essentially considers the expansion to occur without loss of energy, the whole system, chamber and reservoir, being isolated. From the condition of the conservation of mass and energy it may be shown that

\[
\frac{p_1}{p_2} = \frac{\sqrt{\frac{V}{V'}} + 1}{\sqrt{\frac{V}{V'}} + \frac{p'_{2}}{p_{1}}}
\]  

(3.2)

where  
\( V \) = volume of chamber  
\( V' \) = volume of reservoir  
\( p_1 \) = initial pressure in chamber at \( T_1 \)  
\( p_2 \) = instantaneous final pressure in chamber at \( T_2 \)  
\( p'_{1} \) = initial pressure in the reservoir at \( T_1 \)

and the adiabatic law is written in the form

\[
T_1 = T_2 \left( \frac{p_1}{p_2} \right)^{\frac{T_1}{c}}
\]  

(3.3)

\( T_1 \) = initial temperature in chamber  
\( T_2 \) = instantaneous final \( T \) in reservoir.
(3.3) is valid for the *instantaneous* final condition, just prior to condensation, before the system returns to the initial temperature. Since one cannot measure \( P_1/P_2 \) directly, (since the temperature \( T_2 \) is not maintained) it is necessary to estimate the error incurred by allowing the chamber and reservoir to return to room temperature and using the measured final pressure at \( T_1 \) as the pressure \( P_2 \). Two cases are of interest:

1. \( \sqrt{\gamma} \rightarrow \infty \) corresponding to expansion into the atmosphere:
   
   then \( \frac{P_1}{P_2} = \frac{P_1}{P_1^i} \) and the measurement of \( \frac{P_1}{P_2} \) can be made from the initial pressures at the initial temperature.

2. or \( \frac{P_1^i}{P} \rightarrow 0 \) corresponding to expansion into a vacuum.
   
   \[ \frac{P_1}{P_2} \rightarrow 1 + \frac{V_1}{V} \]

   and hence \( \frac{P_1}{P_2} \) is again easily measurable.

The calculations are important with respect to experiments of the Sander and Damköhler type in which one makes simple pressure measurements at the initial temperature and the adiabatic law is assumed. The pressure defined expansion must satisfy one or the other condition in order that a valid application of (3.3) be possible.

The characteristics of the expansion are shown in Figure 5b. Note that the rate of production of the supersaturated state tails off toward the end of the process and hence the attainment of the final temperature is considerably slower than in a volume-defined chamber. Overshoot (and returning puffs of gas when no piston is present) also complicate the actual experiment, giving rise to shock like phenomena (though
Sander and Damköhler report no evidence of overshoot in their work.

Calculations of sensitive times for pressure-defined chambers have not been made but experimental determinations show them to be longer than for a correspondingly large volume-defined chambers (83a).

The most common type of chamber used in nucleation experiments, the piston operated chamber, corresponds to a pressure-defined chamber, since it depends upon equalization of pressure to halt the expansion. The piston merely encloses the vapor under consideration. These are discussed below where a modified expression for $P_1/P_2$ will be developed.

3. Criticism of Earlier Experimental Techniques

No attempt will be made to criticize each experiment in detail, but rather, the general nature of the objections will be indicated in order that factors to be considered in the design of a new apparatus may be clearly outlined. The establishment of a criterion of condensation and the distinction between nucleation and growth have been indicated as difficulties common to all work in nucleation.

The first and most obvious difficulty lies in the assessment of the adiabaticity of the expansion. Once the process has been initiated, heat transfer from the wall tends to offset the cooling. The competition in rates essentially determines the degree of adiabaticity.* The calculations of

* It should be noted that the adiabatic character of the expansion is required only to make possible the determination of $T_2$. 
Williams (81) show that heat transfer varies with \((V/B)^2\) and hence large chambers are desirable. Very small chamber, such as used by Wilson and Powell, depend upon very fast expansions to offset the effect of the wall. The only relevant experimental measurements are those of Volmer and Flood and, for their chamber, the limits of the adiabatic region were indicated. It appears that the assumption of an adiabatic process is not too bad for a large (> 1 liter) chamber (76e).

For pressure-defined chambers, the use of the pressure ratio, measured at the initial temperature, in the adiabatic law must be carefully examined. From the analysis of Herzog (37) it is apparent that unless the reservoir is evacuated or very large, the correct value of \(P_1/P_2\) will not be obtained in experiments of the Sander-Damköhler type.

For those pressure-defined chambers which employ a piston, so that \(V'\) and \(V\) are not fixed, the analysis must be modified. The extent to which the expansion proceeds is fixed by the equality of pressure (ignoring overshoot) but both the final pressures and volumes may vary from those at the condensation point. This situation may be analyzed in the following manner. Consider the processes outlined below:

- **Process A.** The gas in the chamber at \(P_1, V_1, T_1\), connected to a reservoir at \(P'_1, V'_1, T'_1\), undergoes an adiabatic expansion; the gas in the reservoir suffers an adiabatic compression.
The instantaneous process halts when the pressures equalize.*

The adiabatic expansion in the chamber leads to a temperature drop given by

\[ T_2 = T_1 \left( \frac{P_1}{P_2} \right)^{\frac{1}{\gamma}} \]  

(3.4)

Similarly, adiabatic compression in the reservoir yields

\[ T_2' = T_1 \left( \frac{P_1'}{P_2} \right)^{\frac{1}{\gamma}} \]  

(3.5)

Hence

\[ \frac{T_2}{T_2'} = \left( \frac{P_1}{P_1'} \right)^{\frac{1}{\gamma}} \]  

(3.6)

Process B. The chamber, at \( P_2, V_2, T_2 \), warms up while the reservoir at \( P_2', V_2', T_2' \), cools off until at equilibrium they are both at \( P_3, T_1 \) but now occupy \( V_3 \) and \( V_3' \), respectively.

The conservation of mass requires that the following conditions hold:

\[ \frac{P_2 V_2}{T_2} = \frac{P_3 V_3}{T_1} \]

(3.7)

Combining (3.7) with (3.6)

\[ \frac{V_2}{V_2'} = \frac{V_3}{V_3'} \left( \frac{P_1}{P_1'} \right)^{\frac{1}{\gamma}} \]  

(3.8)

But \( V_{\text{Total}} = \text{constant} = V_2 + V_2' = V_3 + V_3' \)  

(3.9)

Hence (3.8) and (3.9) yield

\[ V_2 = \frac{V_T \left( \frac{V_3}{V_3'} \right) \left( \frac{P_1}{P_1'} \right)^{\frac{1}{\gamma}}}{1 + \left( \frac{V_3}{V_3'} \right) \left( \frac{P_1}{P_1'} \right)^{\frac{1}{\gamma}}} \]  

(3.10)

But the conservation of mass requires that

\[ P_2 V_2 / T_2 = P_1 V_1 / T_1 \]  

(3.11)

Combination of (3.11) and (3.10) yields

\[ \left( \frac{P_1}{P_2} \right)^{\frac{1}{\gamma}} = \frac{P_1}{P_3} \left[ \frac{1 + V_3 / V_3'}{(P_1 / P_1')^{\frac{1}{\gamma}} + V_3 / V_3'} \right] \]  

(3.12)

* We are neglecting gravitational effects due to the piston.
Note that this is not a constant energy process, as envisioned by Herzog for the pressure-defined chamber without a piston. The return to the initial temperature (process B) may occur by any means of heat transfer, not necessarily from the hot gas to the cold gas. This is more reasonable when a piston separates the gas volumes.

The two similar cases of interest are:

1. When \( V_3 \to \infty \) (expansion into the atmosphere)

\[
\frac{P_i}{P_2} = \frac{P_i}{P_3} = \frac{V_1}{V_3} = \frac{V_1}{V_3} = \frac{P_1}{P_3}
\]

Since the reservoir (atmospheric) pressure won't be affected by the process.

2. When \( P_1' \to 0 \) (expansion into a vacuum)

\[
\frac{P_i}{P_2} = \left( \frac{V_i}{V_1} \right)' = \left( \frac{V_3}{V_1} \right)' = \frac{V_i}{V_1}
\]

Since when \( P_1' \to 0 \), the expanding gas will occupy the entire volume and \( V_{\text{Total}} = V_3 \).

The error has been calculated for two typical cases (Table 6). Volume is measured in liters; pressure in mm.

<table>
<thead>
<tr>
<th>( V_1 )</th>
<th>( V_3 )</th>
<th>( P_1 )</th>
<th>( V_1 )</th>
<th>( P_1 )</th>
<th>( P_2 )</th>
<th>( \frac{P_1}{P_3} )_{\text{obs}}</th>
<th>( \frac{P_1}{P_2} )</th>
<th>( \Delta )</th>
<th>( \Delta r_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>150</td>
<td>760</td>
<td>134</td>
<td>12</td>
<td>553</td>
<td>570</td>
<td>1.333</td>
<td>1.343</td>
<td>.01</td>
</tr>
<tr>
<td>1.4</td>
<td>4.6</td>
<td>760</td>
<td>5</td>
<td>1</td>
<td>449</td>
<td>542</td>
<td>1.400</td>
<td>1.405</td>
<td>.005</td>
</tr>
</tbody>
</table>

The correction to \( S \) is small but relatively larger for \( T_2 \).

The temporal development of the supersaturation is shown in Figure 5c.

* See section 8.
Another difficulty with pressure-defined chambers, as pointed out by Powell (60), occurs when there is liquid present in the chamber. The expansion tails off at the end and in the last stages the cooling occurs quite slowly. There is a noticeable time lag after the expansion is initiated before condensate is visible. During this time, evaporation of the liquid may occur. It is enhanced by the low pressure existing in the chamber. An increase in the vapor density in this manner would lead to a calculated critical supersaturation ratio which was too low. The extent to which this process occurs cannot be easily estimated on an a priori basis but Powell's data indicates that it could be appreciable if the lag is sufficiently long. Note that this difficulty does not occur inherently in the Wilson-Powell experiments as no time lag exists. The expansion is very rapid, coming to a jarring halt.

The rapid halt raises other problems; splashing of the liquid occurs within the chamber during and at the end of the expansion. This might be confused with the appearance of condensate. Further, evaporation of such spray could yield nuclei (the motes present in the liquid) (90).

A very important experimental parameter is the initial vapor pressure in the chamber. When liquid is present, in time, the equilibrium vapor pressure is reached. When the vapor must be introduced into a flowing gas stream, as in the experiments of Sander and Damköhler, the problem is more complicated as it is difficult to saturate a flowing gas stream
without forming spray (13, 75). One must avoid using any device
which yields spray inasmuch as the droplets form excellent
nuclei and even should they evaporate, the motes of the liquid
might serve as nuclei. Assuming the flowing gas is saturated
may lead to errors.

Last, but by no means least, is the assumption of the
absence of foreign nuclei in the chamber. Obviously, the unsus­
pected presence of such nuclei make the interpretation of the
results quite impossible. It would appear that chambers in
which "cleaning" expansions are used would be free from this
difficulty. Two points, however, indicate possible sources of
difficulty. One is the existence of reevaporation nuclei.
Their presence must be accounted for in some manner else they
remain a possibly unsuspected form of foreign nucleus. They
imply incomplete removal of such nuclei.

The other point, mentioned by Volmer in connection with
his own experiments, but common to all workers (except Sander
and Damköhler, and Pound), is that in each chamber described
the electrodes used to remove ions (which serve as nuclei)
ever encompass the entire chamber. There is always a field­
free space behind or to the side of the electrode. The ini­
tiation of the expansion process sets the gas into rapid
flowing motion. The gas behind or to the side of the elec­
trode then usually enters the region of the field. Prior to
the point at which the expansion is critical for ions, the
latter are swept out as they enter the field. When the ion
limit is passed, the very next ions dragged into the region
cannot be removed - they immediately cause the supersaturated state to collapse. This condensation can occur after the ion limit is passed but before the true supersaturation limit for spontaneous nucleation is reached.* Wilson's postulated production of ions by the expansion process could easily be due to this type of phenomenon.

The experimental findings of Andren on the great difference in the number concentration of observed droplets (as a function of supersaturation) between naturally ionized and artificially ionized gases even in the presence of the same strong electric field indicate that the removal of ions by the field is not complete. The dependence on field strength is to be noted! (See Figure 2).

The discussion of impurity removal from flowing gas streams will be taken up in a later section.

4. The Growth of Droplets

Though the growth of droplets to a visible size from nuclei cannot be measured or computed, measurements on rates of visible droplet growth have been carried out. The importance of this problem has been indicated.

Hazen (33) and Barrett and Germain (5a) have shown that after an uncertain initial period, during which the gas cools, nucleates and the droplets grow to a minimum visible size, the growth law is of the form

* If such a limit exists!
\[
\frac{dr^2}{dt} = K \\
K = \text{constant (3.13)}
\]

Barrett (5b) has shown too that extrapolation of the growth curve toward zero time leads to an intersection with the time axis at \(\sim 0.1\) second after zero. He interprets this as indicating a smaller growth rate during the first 0.1 to 0.2 second and this is in accord with the calculations of Frisch and Collins (24a), and the experiments of Bradley and Evans (10) and Monchick (54) on the evaporation of droplets. The growth (or evaporation) law in these cases is of the form

\[
Qr^2 + Pr = t \quad (3.14)
\]

It is of interest to compute the time required to make a droplet visible assuming the very simple law (3.13) and the initial condition

\[
r(0) = 0
\]

whence

\[
r^2(t) = Kt \quad (3.15)
\]

Experimentally \(K\) is of the order of \(10^{-6}\) cm\(^2\)/second (83b).

For a particle to reach \(10^{-4}\) cm in radius, which should just be visible to the unaided human eye (89), the time of growth is \(\sim 10^{-2}\) seconds. This is a minimum time. Thus the growth time can be appreciable, and the supersaturated state must be maintained for at least an equivalent length of time.

5. Description of the Apparatus

a. Design Factors

From the foregoing discussion, certain factors in the design of a cloud chamber are clearly desirable and they may be summarized as follows:
1. The chamber should be large to avoid wall effects which might tend to interfere with the adiabaticity.

2. No liquid should be present in the chamber. This implies the purification and saturation of a flowing gas must be accomplished.

3. A rapid expansion is desirable.

4. A direct measurement of $r_e$ should be made, yet the jarring shock phenomena of volume-defined expansions should be avoided. The tail effects of the pressure-defined chamber should be avoided, if possible. This implies that the measurement should be made during the expansion.

5. The electric field should encompass the entire region.

6. It would be preferable to use some non-subjective viewing device for the detection of condensate to avoid the inherent difficulties of visual observation.

b. The Cloud Chamber

With the foregoing factors in mind, the chamber shown in Figures 6a, 6b and 7 was designed.* It consists basically of two parts: the upper "cloud chamber" (CC) over a larger "piston chamber" (PC).

The lower piston chamber, of cast iron, consists of a hollow cylinder 16" high and 14" in outside diameter with a wall thickness of $\frac{3}{4}"$. There is a low-carbon steel cone (Q)

* Fabricated by the Waltham Model Works, Waltham, Mass.
inside the cylinder, through the axis of which passes a 1" opening (K) which allows connection to a vacuum reservoir. The whole assembly was black-enamed. and baked (to remove the solvent oils).

There is 250 lbs of mercury (C) in the cylinder in which floats a close fitting 10 lb low-carbon steel piston (B) (8" high, 12 15/16" in diameter). The latter has been painted black (and baked) and 1/8" from the top, a yellow line (H) passes circumferentially. The cone serves to minimize the volume of mercury which acts to seal the space under the piston from the cloud chamber itself. The mercury can be drained out through the outlet J.

On the side of the piston chamber there is a window (D) (6" long, 3/4" wide) through which the piston, and particularly the yellow line (H), are made visible.

The cloud chamber (CC) consists of a cylinder formed from the brass plate X (12" in diameter and 1/4" thick), the two glass rings (R) (14" outside diameter, 4" high and 1/4" thick) which are separated by a 2" high cast bronze ring (S) and a lower brass ring (L) (14" outside diameter, 9 3/4" inside diameter, 1/4" thick). The pieces are held together by means of tie rods (T) (which pass outside the chamber) and the ring (L) is screwed onto the piston chamber to complete the assembly. Gaskets between each piece serve to make the whole vacuum tight; insulating bushings on the tie rods in X and L (the latter sealed with beeswax-rosin) allow a voltage
difference to be applied between these plates.

The cast bronze ring (S) has mounted on it, at 90° intervals, four 1" windows (optical flats) on two of which (90° apart) are mounted a collimated light source (U) and a photomultiplier tube (P)*. In addition, there are four ¼" brass tubes (V), to each of which a three way, 4mm stopcock is sealed (with rosin-beeswax), for the introduction of the carrier gas and vapor. To one of these a manometer is permanently attached.

c. The Optical System

The light source is shown in detail (to scale) in Figure 8.** It consists of a 150 watt projection lamp (P) mounted in an aircooled*** holder with a light-baffle cap (C). The lamp is located at the focus of a mirror (M) which collimates the beam, passing it through a heat absorbing optical flat (H). Further collimation is secured by means of lens (L). The mirror is adjustable and the whole lamp housing slides along the tube (T) to make further adjustments possible. The whole assembly (of brass, and oxide coated) is bolted onto the

* These will be described more carefully in the next section.

** We gratefully acknowledge the assistance of the staff of the Waltham Model Works in the design of the housing for the light source and the photomultiplier tube.

*** By a blower not shown.
LIGHT SOURCE

FIGURE 8
window \((W)\) which is in turn bolted onto the central bronze ring \((S)\).

The window, a \(1''\) optical flat \((OF)\), is made vacuum tight by means of two "O" rings at 0 and 0'.

The light stop \(B\) allows only a one-half inch circular collimated beam to enter the chamber. To reduce internal reflection, the beam is passed out of the chamber through the window at \(180^\circ\).

The lamp was initially operated by a DC power supply to eliminate spurious AC signals to the phototube. In later work, this light source was removed and an AC American Optical Company microscope lamp was substituted. The heat absorbing flat \((H)\) was removed (by unscrewing the plug \(R\)) and used to form one end of a \(4''\) cylindrical cell containing a \(2\%\ CuSO_4\) solution, the end of which was placed at the dotted line. The lamp was placed at the other end. There was no detectable difference in performance.

The 1P21 photomultiplier housing is shown in Figure 9 (to scale). The mounting, similar to the light source, contains a lens \((L)\) designed to focus the radiation from the center of the collimated light beam onto the photosensitive target, \((T)\), of the 1P21. A dark stop \((D)\) permits only a \(\frac{3}{8}''\) circular beam to be seen by the target \((T)\). Thus, a volume of about \(1/8\) cubic inch is viewed by the photomultiplier tube.

The phototube was shielded and coaxial cable \((RG\ 59U)\) and connectors were used exclusively. A standard 1P21 photomultiplier resistor circuit was used \((91)\) together with a
regulated high voltage supply (Figure 10). The tube was operated with about 90 volts across each dynode, a total of 950 volts.

d. Mode of Operation

The experiment consists in the photographic recording of the temporal displacement of the piston and the correlation of that displacement with the appearance of scattering due to condensate in the chamber. The scattered light is monitored by the photomultiplier tube, the output of which is suitably recorded. The condensation occurs during the expansion rather than at the end, as in previous investigations, but the relevant parameters are measureable.

The detailed operation consists in elevating the piston (by means of air admitted through stopcock (W), (Figure 7)) to some desired initial position and charging the chamber with vapor and carrier gas by flushing through the ports (V) until the foreign nuclei are removed.* The initial position is then recorded with the camera (E)** by photographing the yellow line (H). The expansion is initiated by opening the valve (I) (a quick opening valve) to the vacuum reservoir (a 120 liter steel tank), which causes the piston (B) to descend rapidly, expanding the gas above it.

When the valve (I) is opened, the mercury switch (M) is

*This is discussed in section 7b.

**Crown Graphic 4 x 5.
activated completing the circuit between Z and Z' (after an unknown fraction of a second) and causes two processes to be initiated simultaneously:

1. The strobolux (F), a high intensity stroboscope (General Radio 648A) which is held just below its striking potential, is activated and illuminates the yellow line on the moving piston at 1/50 of a second intervals. (It is driven by a strobotac, General Radio 631-B). The successive positions of the piston are recorded (by an open-flash technique*) with the camera (E).

2. The output of the LP21 photomultiplier tube is connected to the vertical plates of a high voltage oscilloscope (Dumont 250AH) through the oscilloscope DC amplifier. The instrument is designed for an externally triggered sweep and the closing of switch (M) initiates that sweep causing the amplified output to be displayed on the oscilloscope screen. This output is recorded by an oscillographic camera (Dumont Type 296). When condensate appears, the scattering due to the droplets is reflected in an increased current output from the LP21 and a "break" appears in the horizontal sweep. (See Figure 19).

The strobolux pulses are also detected by the LP21 and

* The whole process is carried out in a darkened room.
appear as vertical markers on the relatively slowly varying horizontal sweep. A direct correlation between the piston position and the appearance of condensate is obtained. The expansion ratio is obtained from a previous calibration of the distance on the photograph (from camera (E)) as a function of \( r_e \).

A DC voltage could be applied between the roof of the cloud chamber and the base which provided a field strength of either 30, 60, or 90 volts/cm. A standard DC power supply was used for this purpose.

In order to prevent undue overexposure of the film* in camera (E) the flashing of the strobolux was controlled by an interval timer which, once having initiated the timing cycle (via the Hg switch), allowed flashing for some definite fraction of a second, then turned off the stroboscope and prevented any reinitiation of the sweep of the oscillograph (preventing double exposure on the oscillograph as well).

Its essential operation consisted in removing a short circuit between the strobolux and the driving oscillator for a fixed length of time. The circuit is shown in Figure 11.

Since the expansion ratio may be expressed in the form

\[
 r_e = \frac{V_2}{V_1} = (\frac{V_1}{V_1} + \alpha h) \frac{V_1}{V_1} = 1 + \alpha h / V_1
\]

(3.16)

where \( h \) is the descent of the piston (as measured, for example, on the photograph), and \( \alpha \) some geometrical factor related to the cross sectional area of the piston chamber, it is necessary to fix the initial piston position quite exactly. This

---

* DuPont High Speed Pan (#428).
was accomplished in the following manner: two glass slides separated by 1" spacers had lines scratched \( \frac{1}{4} \)" from their upper edges. This assembly was pressed against the window (D) and the yellow line (H) was aligned with the two scratches (see Figure 12). The reproducibility of the initial piston setting was checked manometrically and found to be reproducible to within one mm. This leads to an error in \( V_1 \) of about \( .06 \) liters. If \( h \) is measured as the distance on the photographic plate, \( \alpha \approx .9 \). The error in \( r_e \) is then \( \approx .003 \).

The initial temperature of the gas was obtained by measuring the initial temperature of the chamber, the mass of which, relative to that of the gas, is sufficient to insure its action as a heat reservoir. The entire room was air conditioned and to insure uniformity of temperature, electric fans were employed as stirrers, one of which blew on the chamber. This uniformity was checked with thermocouple measurements at 7 points on the chamber and two thermometers at the top and bottom of the cloud chamber. Once the proper location of the fan was found, the thermometers served to indicate the temperature. The experiments were carried out in the steady cycle of the air conditioning unit, insuring thermal equilibrium.

6. Water Vapor Saturation and Analysis

It is desirable in the saturation of the carrier gas

---

* The thermometers were compared with a standard thermometer and found to be quite satisfactory.
FIGURE 12

SETTING OF PISTON
stream for nucleation experiments to avoid the production of spray. To this end, the saturator shown in Figure 13 was built in which the gas passes over the surface of the water and accumulates vapor. The system was designed to allow any mixture of dry N₂ and nearly saturated N₂ (at the temperature of the thermostat bath) to be reproducibly obtained and, hence, a wide range of vapor pressures can be obtained. Time must be allowed for a steady state water vapor concentration to be reached. When this is done, the use of the saturator alone, for example, delivers a vapor nearly saturated. The flow meters were calibrated by emptying an inverted carboy of known volume but no pressure corrections were made. Absolute rate of flow was not important—only constancy and reproducibility. A standard N₂ reducing valve was sufficient to hold a steady flow.

One cannot calculate the vapor pressure in such a system since the degree of saturation is unknown and, accordingly, a convenient system for water vapor analysis was developed.

The method depends upon the reaction of concentrated H₂SO₄ with H₂O vapor.* The apparatus is shown in Figure 14. A sealed fragile bulb filled with concentrated H₂SO₄ (C) was placed in the bottom of the analysis flask. The carrier gas and vapor entered through arm 1 and passed through the flask, through the manometer, and out of arm 3. When a sample was to

* The use of this reaction has been previously reported (43, 63, 71) but the specific form is new and quite important.
A water vapor analysis flask

Figure 14
be collected, Hg was poured into arm 3 until the system was sealed. The gas was then allowed to flow out arm 2. The rest of the Hg was poured in and then the system isolated by shutting stopcock A and connecting stopcock B back to the manometer. This eliminated any spurious sample collection in the manometer arm. The flask was then immersed in a thermostatted bath, the initial heights of the Hg in the manometer recorded and the bulb broken. After about 1 hour, all the water was removed and the pressure change noted. The latter, corrected for atmospheric pressure fluctuations and in some cases for the decrease in volume due to the rise of Hg in the manometer, yields directly the vapor pressure of H$_2$O, the quantity of interest. Two sizes of analysis flasks were used, 500 and 1000 cc to check on dilution errors.

The method was tested by placing two 5 cc bulbs of H$_2$SO$_4$ in a flask in which a third 3 cc bulb of H$_2$O could be broken with a plunger. The water bulb was broken in the thermostat and then after 1.5 hours the H$_2$SO$_4$ bulbs were broken. As an example of the results:

<table>
<thead>
<tr>
<th>Initial pressure difference before any bulbs broken</th>
<th>$\Delta P$</th>
<th>Atmospheric Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.17 mm</td>
<td>765.2 mm</td>
<td></td>
</tr>
</tbody>
</table>

| Final pressure difference after all bulbs broken     | $\Delta P = -0.52$ mm | 764.8 mm |

| Final corrected pressure difference                  | 15.25 mm            |

The error is $\sim 0.1$ mm, which approximately that due to the
determination of atmospheric pressure. The partial pressure of water over a solution of 10cc H$_2$SO$_4$ and 3 cc water is $<0.1$ mm (88).

Dynamic checks for consistency were carried out by passing the sample simultaneously into four analysis flasks for 2½ hours; the saturator bath was at 20.4°C, the flow 1 liter/minute. Sampling was at 2 minute intervals.

<table>
<thead>
<tr>
<th>Volume</th>
<th>Vapor Pressure of H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 500 cc</td>
<td>16.7 mm</td>
</tr>
<tr>
<td>#2 500 cc</td>
<td>no analysis</td>
</tr>
<tr>
<td>#3 1000 cc</td>
<td>17.4 mm</td>
</tr>
<tr>
<td>#4 500 cc</td>
<td>16.8 mm</td>
</tr>
</tbody>
</table>

The result obtained with the large flask was due to a dilution error. Note that the saturation pressure at 20.4°C is 17.97 mm.

With two flasks in parallel a flow of 1.5 liter/minute, and the saturating bath at 20.3°C (vapor pressure 17.86 mm):

| #1 500 cc | 17.0 mm |
| #2 500 cc | 16.8 mm |

The measurement was repeated immediately afterward (with larger bore stopcocks on the analysis flasks):

| #1 500 cc | 16.9 mm |
| #2 500 cc | 16.8 mm |

It is apparent that the vapor pressure averages about 1 mm under saturation when a steady state is reached. The diluting system was checked for consistency using two flasks in series. The results for dry N$_2$ plus nearly saturated N$_2$ and a bath temperature of 20.5°C were

| #1 500 cc | 4.9 mm |
| #2 1000 cc | 4.8 mm |
and with four in parallel with decreased dry N₂*

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>500 cc</td>
<td>7.0 mm</td>
</tr>
<tr>
<td>#2</td>
<td>500 cc</td>
<td>6.8 mm</td>
</tr>
<tr>
<td>#3</td>
<td>500 cc</td>
<td>6.9 mm</td>
</tr>
<tr>
<td>#4</td>
<td>1000 cc</td>
<td>8.3 mm</td>
</tr>
</tbody>
</table>

The importance of dilution effects, as evidenced in the results obtained with the larger flask, is clear. The manometer correction due to the volume change is usually less than .1 mm as can be seen from the following analysis:

If \( p_m = p_i - p_{N_2} \)
and \( p_i = p_{H_2O} + p_{N_2} \),
then \( p_{H_2O} = p_m - p_{N_2} + p_{N_2} \).

But \( p_{N_2} = p_0 \left[ V_0 - \frac{\pi r^2 h}{V_0} \right] \)
where \( r = \) radius of manometer tube, \( h \) the rise in the height of mercury in the manometer arm connected to that flask, \( V_0 \) the initial volume.

Then \( p_{H_2O} = p_m + p_{N_2} \left[ \frac{\pi r^2 h}{V_0} \right] \) (3.17)

For .6 cm diameter tubing, \( \pi r^2 h = 0.283h \) cc. For \( V_o = 500 \) cc, the corrections are tabulated below.

<table>
<thead>
<tr>
<th>( h ) cm</th>
<th>( p_{N_2} ) ( .3h/V_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( p_{N_2} ) mm.</td>
</tr>
<tr>
<td>1</td>
<td>.05</td>
</tr>
<tr>
<td>2</td>
<td>.09</td>
</tr>
</tbody>
</table>

* The absolute flows were not measured.
(For a 1000 cc. flask, the correction is halved). These corrections have been included in all the foregoing.

7. The Purification of Nitrogen

a. General Considerations

It is clear that in an investigation of spontaneous nucleation, the primary experimental requirement is the absolute purity of the carrier gas and vapor. Purity, in this sense, implies removal of all nuclei capable of initiating the condensation process. Their unsuspected presence could easily invalidate the theoretical interpretations.

Purification, as the term will be employed here, involves the following processes:

1. Removal of condensable vapors which might serve as nuclei or take part in a binary nucleation process (66a).
2. Removal of particulate matter which could catalyse the condensation.
3. Removal of ions, large or small, which act as nuclei.

The usual scheme for effecting this purification consists in the freezing out of condensable impurities in suitable traps and the filtration or deposition of particulate matter by or on suitable surfaces. Ion removal is accomplished by the application of an electric field to the region. Though adequate theoretical analyses of these situations are lacking and the experimental data is very meagre (in the concentration range of interest), it is possible to examine the physical processes and draw qualitative conclusions.
Consider the condensation of a vapor in a cold trap. The principle of operation is the creation of a sharp concentration gradient between the vapor in the gas stream and the walls of the trap so as to force the vapor to diffuse to the colder trap wall. If the temperature gradient is too sharp, the vapor will cool before diffusion to the wall can become appreciable and condensation in the gas stream (aerosol formation) may occur. In general, there will be a competition between diffusion to the walls and nucleation. The temperature gradient and flow rate essentially determine the cooling rate which in turn determines which process will occur.

It is possible to preferentially influence one or the other of these processes. If the wall is moved closer to the vapor (by packing the trap) the distance a molecule must diffuse is lessened; the linear flow velocity, however, goes up and some compromise must be reached. The presence of foreign nuclei in the vapor stream makes the process of aerosol formation much easier as the supersaturation required to cause condensation on foreign nuclei is lower than for spontaneous nucleation. The aerosols are not removed by the trap! (9).

One point is clear: other factors being equal, a more efficient trapping of the vapor may result from the use of a "warmer" cold trap. The higher the vapor pressure the more important will be the effect.

Experimentally, this problem has been studied by Bircumshaw (9), Goldman and DallaValle (29) and recently by
Mizushino, Nakajimana, Omoto, and Fukusen (53). Theile (72) has reviewed the subject and essentially confirms the ideas outlined above. Thus, he found that foreign nuclei were necessary to cause fog formation in traps and filtration of the gas could reduce or eliminate the fog.

The only theoretical approach based on similar ideas was that of Amelin and Borodastova (2). Their calculation indicated that though 15 mm of ethanol in air would be completely trapped when the trap temperature was $>-33^\circ C$, 70% of the vapor would be lost at $-80^\circ C$. This analysis is, however, unrealistic in that foreign nuclei are not considered. The authors reach a similar conclusion about increasing the efficiency of the process by using warmer traps or a series of progressively colder traps.

The problem of the removal of particulate matter from air streams has been thoroughly treated in the Handbook on Air Cleaning of the U.S. Atomic Energy Commission (85a). The methods involve applying forces to the particles to cause them to move to the collecting surface and include inertial, diffusional, electrical and thermal forces.

Fibrous filters, such as cotton and glass wool, depend upon the inertia of the particle to cause impaction on the fiber. The finer the fiber, the higher the impaction efficiency. Clearly, a longer filter is more efficient in the random process of impaction.

Paper filters are thought to act by means of electrical forces as well as impaction.
In general, very fine glass wool and CC-6 filter paper* are about 99.99% efficient in removing particles between 1 and \( .1 \mu \) radius but unfortunately, particles of \(< .1 \mu \) may still be very active catalysts. Since they cannot easily be sampled, the real efficiency is not known (85b).

Electrostatic and thermal precipitators share the disadvantage of not binding the particles precipitated, so that blow-off results; their real efficiency for our purpose is not known since it is the extremely minute traces of invisible particulate matter which are important.

A fundamental difficulty in this work is that no good method has been developed to analyze for the concentration of vapor and particulate matter in which we are interested; one can only guess at the upper limit of impurities present but there is no knowledge of the upper limit tolerable.

It has been pointed out that ions can and do serve as nuclei. The usual scheme of removal is the simple application of a strong electric field to the region but the efficiency of this process depends upon the mobility of the ion (its mass and charge) and its dielectric character. If the charge would remain on the ion, the field would hold it on a plate. If it discharges, it may fall off or be blown off.

The sizes of ions range from \( 10^{-7} \) to \( 10^{-5} \) cm. in diameter and their mobility varies accordingly (89b). It is

difficult to estimate the efficiency of ion removal by the
application of a field. The results of Andren indicate it is
not as straightforward a process as it might seem at first.

b. Criterion of Purity

It will be well at this point to indicate the method used
to infer purity of the gas. At the outset it must be admitted
that the method is subjective and requires subjective inter-
pretation of observed phenomena. Nonetheless, it is at least
an indication of the degree of purity.

In essence, the method consists in observing in an aux-
iliary chamber (Figure 15) the condensation process and from
the nature of the results, the "purity" may be inferred. The
saturated gas is led into the lower flask, the 3 upper flasks
serving as the vacuum reservoir. The following observations
are noted:

a. Initially, when the gas has not been flowing through
the cleaning system for any length of time, immediately
upon opening the stopcock connecting the flask to the
reservoir, a dense cloud is obtained with rather
small droplets.

b. In time, formation of the cloud does not occur at the
instant the stopcock is opened but some one second
later. This cloud forms sharply, with few but large
droplets.

c. Occasionally, one sees a single very large droplet
fall rapidly to the bottom and nothing else. Some-
times a few (2 or 3) droplets form immediately, fall out and a second cloud appears with few but not too large droplets ("double cloud").

These results are interpreted as follows: initially, the vapor has condensation nuclei. The saturated gas is cooled as soon as the stopcock is opened; the condensation nuclei act and a fine dense cloud forms (a). In time, the nuclei are removed and then considerable supersaturation must exist before condensation will occur. The rate of cooling is governed by the rate of efflux of the gas through the stopcock. Since the chamber is pressure-defined, this rate diminishes near the end of the expansion and considerable time must elapse prior to reaching the temperature for spontaneous nucleation; hence the time lag (b). The last observations (c) are striking illustrations of what a single condensation nucleus may do! Even a few will complicate the phenomenon.

The criterion chosen was to observe absolutely nothing for ~ 1 second and then sharply defined condensation. The test chamber was at an exit port of the large cloud chamber and in this manner one could tell when the large chamber was clean.*

c. Description of the Purification Systems

The first cleaning system built (Figure 16) proved to

* It is clear that this method cannot be used on unsaturated vapors. One must always test a saturated vapor.
FIGURE 16

NITROGEN PURIFICATION LINE

GLASS WOOL
GLASS BEADS
-80

TO SATURATOR

N2
be remarkably efficient being, in fact, one of the few which worked at all. N₂ (oil pumped) was passed into a tube containing glass wool (20°C) and cold glass beads (-80°C). The former served to remove condensation nuclei (and raise the critical supersaturation ratio for vapors), the latter increases the cold wall surface (and so reduced the diffusion distance). The gas then passed into a cold copper coil (copper being a very efficient heat exchanger) and then into a 4 ft. cotton filter. On the outlet side a safety "T" with a blow out plug was placed. The gas then passed into a medium porosity 4" sintered glass filter funnel. Passage through a trap and cooling coil completed the purification. The carrier gas then entered the saturator.

This line was remarkably successful for a period of over four months. In that time, the saturator "went bad" once and the cotton filter had to be replaced once. When the system failed, all efforts to track down the cause were unsuccessful. Minor modifications such as changing shape, path length and packing of traps were not successful. Complete rebuilding of the line was similarly unsuccessful.

Line number IV (Figure 17) represented a second successful cleaning system. Essentially, the impurity was oxidized with hot CuO; hot Cu was used to remove excess oxygen. Activated silica gel was used to take up water.* The heated traps were at -80°C.
HEATERS

NITROGEN PURIFICATION
LINE IV

TO SATURATOR

FIGURE 17
traps, (H), added to break up aerosol which might have been formed, were superfluous. Both oil pumped and water pumped \( \text{N}_2 \) were used. The line was erratic and only worked for a few weeks. On occasion, however, it worked without the oven.

Modifications attempted in Line IV included:

a) Using glass wool filters as traps at \(-80^\circ\) and \(-169^\circ\) C.

b) Using trap temperatures of \(-169^\circ\) C.

c) Graded cooling of traps (ice and salt, dry ice and trichloroethylene, liquid \( \text{N}_2 \)).

d) Insertion of various paper filters (6C6 paper).

Attempts to rid the gas of nuclei by charging it with water vapor before passage into the traps, under a very sharp temperature gradient, were not successful due to rapid clogging of the traps with ice.

A close copy of the initial line, using liquid \( \text{N}_2 \) as the carrier gas source, again proved successful and Volmer-type measurements were carried out (Figure 18). A manostat (M) controlled the heater in the liquid \( \text{N}_2 \) and kept a quite steady flow of \( \text{N}_2 \).

The conclusion reached as to the cause of the inability to consistently obtain pure \( \text{N}_2 \) was that the removal of particulate matter was incomplete. Fortuitous packing of the filters was probably responsible for the success of the various lines. The oven aided by burning out these impurities since it always improved the situation. The degree of improvement with increasing oven length was negligible (from 6"
TO RELAY

TO RELAY

800 C

CuO

GLASS WOOL

GLASS WOOL

COTTON

TO SATURATOR

NITROGEN PURIFICATION LINE XI

FIGURE 18
to 18°). In the last line, however, the cooling of the traps was very important indicating possibly that a condensation process was involved though mass spectra taken of samples indicated no impurity! The impurity is probably present in concentrations of less than 1 part in $10^6$.

An electrostatic precipitator was built but the results were unsuccessful.

8. Error Analysis

It is of interest to compute the degree of experimental precision required in the measurement of the relevant variables assuming an ideal experiment where the supersaturation would be given by Equation (2.1). The measured variables are the initial pressure, $P_1$, the critical expansion ratio, $r_e$, and the initial temperature, $T_1$, (from which $T_2$ and $p_\infty(T_2)$ are then determined).

Thus 

$$S = S(P_1, r_e, T_1) = \frac{P_1}{P_\infty} r_e^{-\gamma} \quad \text{[where } P_\infty = P_\infty(T_1, r_e)\text{]} \quad (2.1)$$

The total differential of $S$ is

$$ds = \left(\frac{\partial S}{\partial T_1}\right)_{P_1, r_e}dT_1 + \left(\frac{\partial S}{\partial r_e}\right)_{P_1, T_1}dr_e + \left(\frac{\partial S}{\partial P_1}\right)_{T_1, r_e}dP_1 \quad (3.18)$$

For finite changes in the variables (21a)

$$\Delta S \approx \left|\frac{\partial S}{\partial T_1}\right|\Delta T_1 + \left|\frac{\partial S}{\partial r_e}\right|\Delta r_e + \left|\frac{\partial S}{\partial P_1}\right|\Delta P_1 \quad (3.19)$$

Since

$$ \left(\frac{\partial S}{\partial T_1}\right)_{P_1, r_e} = -\frac{P_1}{P_\infty} r_e^{1-\gamma} \left(\frac{\partial P_\infty}{\partial T_1}\right)_{P_1, r_e} = A \quad (3.20) $$

$$ \left(\frac{\partial S}{\partial r_e}\right)_{P_1, T_1} = -\gamma r_e \left(\frac{P_\infty}{P_1}\right) r_e^{-1} - \frac{P_1}{P_\infty} \left(\frac{\partial P_\infty}{\partial T_1}\right)_{P_1, r_e} T_1 (1-\gamma) r_e^{-\gamma} = B \quad (3.21) $$

* By Dr. M. Zelikoff, Air Force Cambridge Research Center.*
\[
\frac{\partial S}{\partial \phi_c} \bigg|_{T_1, r_e} = \frac{r_e}{\rho_\infty} = C \quad (3.22)
\]

\[
\Delta S = |A \Delta T_1| + |B \Delta r_e| + |C \Delta \phi| \quad (3.23)
\]

Three typical cases have been tabulated (Table 8).

The error in \( S \) due to errors in \( p_1, r_e \) and \( T_1 \) may be easily estimated from Table 8. Thus, if the precision in \( T_1 \) is \( \pm 0.1^\circ \), \( r_e \pm 0.001 \), \( p_1 \pm 0.1 \) mm, then the error in \( S \) is 2\%.

If, however, the measurement of \( T_1 \) is \( \pm 0.5^\circ \), \( r_e \pm 0.01 \) and \( p_1 \pm 0.5 \) mm, the error in \( S \) is about 13\%.

Since the usual representation of the data plots \( S \) vs \( T_2 \), it is of interest to examine the error in \( T_2 \) due to the errors in \( T_1 \) and \( r_e \). \( T_2 \) is given by Equation (2.2) and by a similar process to that illustrated by Equation (3.18) to (3.23) one obtains

\[
\Delta T_2 \leq |r e^{1-1} \Delta T_1| + |T_1(1-t) r e^{1-1} \Delta r_e| \quad (3.24)
\]

\[
\leq \frac{1}{A} \Delta T_1 + |B \Delta r_e| \quad (3.25)
\]

Typical cases are shown in Table 9.

<table>
<thead>
<tr>
<th>( r_e )</th>
<th>( T_1 )</th>
<th>( A )</th>
<th>( B )</th>
<th>( \Delta r_e )</th>
<th>( \Delta T_1 )</th>
<th>( \Delta T_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.32</td>
<td>294.7</td>
<td>.90</td>
<td>80.4</td>
<td>.01</td>
<td>.5°</td>
<td>1.2°</td>
</tr>
<tr>
<td>1.41</td>
<td>296.3</td>
<td>.877</td>
<td>72.8</td>
<td>.01</td>
<td>.1</td>
<td>.2</td>
</tr>
</tbody>
</table>

The errors in \( T_2 \) may be appreciable when the error in \( r_e \) is \( \sim .01 \). On a percentage basis, however, the error is not large.
TABLE 8

Error Analysis

<table>
<thead>
<tr>
<th>$T_1^\circ K$</th>
<th>$r_e$</th>
<th>$p_1$(mm)</th>
<th>$S_{ideal}$</th>
<th>$A^*$</th>
<th>$B$</th>
<th>$C$</th>
<th>$\Delta T_1$</th>
<th>$\Delta r_e$</th>
<th>$\Delta p_1$</th>
<th>$\Delta S$</th>
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<tr>
<td>294.7</td>
<td>1.32</td>
<td>14.5</td>
<td>4.43</td>
<td>-304</td>
<td>21.5</td>
<td>.305</td>
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<td>1</td>
<td>.61</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>.1</td>
<td>.01</td>
<td>1</td>
<td>1.14</td>
</tr>
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<td>295</td>
<td>1.38</td>
<td>16.0</td>
<td>6.79</td>
<td>-.40</td>
<td>23.9</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>.1</td>
<td>.01</td>
<td>1</td>
<td>.70</td>
</tr>
</tbody>
</table>

* $A$, $B$, and $C$ are quantities defined by Equations (3.20), (3.21) and (3.22).
9. Results

Three types of measurements were carried out:

1. Nucleation of supercooled water vapor in the presence and absence of an electric field (using N₂ as a carrier gas) observing the formation of condensate by means of the photomultiplier tube.

2. Nucleation of supercooled water vapor in the presence of an electric field using the classical technique of ever-increasing expansion with visual observation.

3. Studies of the nucleation of water vapor by foreign nuclei in an attempt to assess the validity of the adiabatic hypothesis.

a. Nucleation in the Absence of an Electric Field

The early experiments were carried out under somewhat crude conditions but the results are still meaningful, though subject to a larger error than the later work.

The technique of the measurement differed from the general scheme outlined previously in the following respects:

1. The initial position of the piston was fixed by aligning the yellow line of the piston with a scale on the window, by observation on the ground glass screen of the camera (E).

2. The photomultiplier tube, a 1P21, was powered by 4 Burgess 300 volt batteries (#U-200), a total of 1200 volts (120 volts/dynode).

3. The projection lamp (150 watts) was powered by two
Burgess 45 volt batteries (# 5308) in series.

4. The saturator was a smaller version of the one shown in Figure 13 consisting of six \( \frac{3}{4} \) liter round bottom flasks, half filled with distilled water. There was no diluter.

5. The vapor pressure of water in the carrier gas was not measured. Accordingly, some reasonable value must be assigned to this parameter.

From the data on the larger saturator, which device produced a vapor pressure some 1 mm under saturation (with reference to the saturator bath temperature) it would seem likely that the vapor pressure of the gas from the smaller saturator would be even lower. One measurement of the vapor pressure was made (the saturator bath was at 19.0°C and the flow \( \frac{3}{4} \) liter/minute) and it was found to be 15.6 mm; saturation would be 16.5 mm. The relatively high vapor pressure is undoubtedly due to the low flow rate, a condition not met in the actual experiments. Accordingly, the results tabulated are calculated on the basis of an assumed vapor pressure taking into account the flow rate, the length of time the chamber was flushed and the saturator bath temperature (since the carrier gas is more easily saturated at lower temperatures). It should be noted that an error of \( \pm 1 \) mm in the vapor pressure results in only about 10% error in \( S_{\text{critical}} \).

The photographic results are shown in Figures 19 and 20 while the analysis of the data is given in Table 10.
<table>
<thead>
<tr>
<th>Run #</th>
<th>$T_1$°K</th>
<th>Saturator Bath Temperature in °C</th>
<th>Flushing Time and Rate</th>
<th>Maximum Vapor Pressure in mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>296.2</td>
<td>18.5</td>
<td>-</td>
<td>15.97</td>
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<td>5 March 51</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3A</td>
<td>294.7</td>
<td>18.0</td>
<td>3 hrs 1.5 lit/min</td>
<td>15.48</td>
</tr>
<tr>
<td>14 March 51</td>
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<td></td>
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<td></td>
</tr>
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<td>4A</td>
<td>296.2</td>
<td>18.0</td>
<td>1.5 hrs 1.5 lit/min</td>
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</tr>
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<td>15 March 51</td>
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<td>5A</td>
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<td>18.0</td>
<td>3 hrs 3/4 lit/min</td>
<td>15.48</td>
</tr>
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<td>15 March 51</td>
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<td></td>
</tr>
<tr>
<td>9A</td>
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<td>19.0</td>
<td>2 1/2 hrs 1 lit/min</td>
<td>16.48</td>
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<td>3 1/2 hrs 3/4 lit/min</td>
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<td>0.0</td>
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<td>0.0</td>
<td>-</td>
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### Runs 1A - 14A

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<th>Number of Pressure Pulses</th>
<th>Distance (cm.)</th>
<th>( r_{\text{crit}} )</th>
<th>( T_2^0 )K</th>
<th>( P_{\text{crit}}(T_2) ) in mm.</th>
<th>( S_{\text{crit}} )</th>
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<td>244.2</td>
<td>.52</td>
<td>4.5</td>
<td>14A</td>
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</table>

* When \( d > 10 \) cm, the densitometer traces were used.
The photographic results were interpreted by enlarging the oscillograph and visually estimating the minimum number of pulses from the initial pulse to the "break" which indicated that condensate had appeared. In some cases, the counting was done from the last pulse backward to insure that no error would be made in locating the initial pulse.

Having obtained this number of pulses, the piston photograph was used to obtain the expansion ratio at the point where the scattering began (using a previous Boyle's Law calibration). The measurement of distance on the piston photograph was carried out initially with a measuring microscope directly on the negative but later, densitometer traces were made of the negatives and a calibration in terms of distance on the densitometer record was used to compute $r_e$. Both direct measurements and densitometer traces were used to check the calculations.

The following points are to be noted about the various runs:

**Run #3A** - The pulses ended prior to the "break". The temporal similarity between the motion of the piston in Run #1A and #3A is striking; five lines superimpose exactly. Accordingly, the piston photograph of #1A was used to extrapolate that of #3A. The extrapolation of the oscillograph is rigorously valid inasmuch as both the spacing of the pulses and the sweep of the oscilloscope are quite uniform.

**Run #5A** - Extrapolation of #5A had to be carried out in a similar fashion to #3A. Here, #4A was used as the model.
Runs # 11A, 12A—The "break" was obtained by counting backward from the final pulse to avoid any uncertainty in the initial pulse. The saturator bath temperature was changed between runs # 10A and 11A. Accordingly, due to the short flushing time, the vapor pressure in the chamber for run #11A may be higher than the saturation vapor pressure. #12A should be more nearly normal.

Runs # 13A, 14A—Since the saturator bath temperature was again lowered, preliminary flushing was necessary. The vapor pressure for #13A may be higher than saturation, with #14A being more nearly at the saturation vapor pressure (at 0°C).

The results are graphically illustrated in Figure 29 along with those of other investigators. It appears that they are essentially in agreement with previous results for condensation on ions (in the absence of an electric field). The discussion, however, will be deferred until all the results have been presented.

b. Nucleation in the Presence of an Electric Field

The next set of experiments was carried out with the electric field connected across the upper plate of the chamber, X, (Figure 7) and the lower brass plate, L. The piston makes electrical contact with the piston chamber (and L) through the mercury (C). The technique of the measurement is that described below (section 5d).* All the measurements were

* The new method of fixing the initial position of the piston necessitated a new calibration.
made at the same field strength, 60 volts/cm.

The photographic data are shown in Figures 21 and 22 and the analysis is given in Table 11.

In general, where two water vapor analyses were carried out, the two results being denoted by #1 and #2, the two flasks were in series at an exit port of the chamber, with flask #2 being closer to the chamber and probably representing more precisely the vapor pressure in the chamber for the particular experiment. When the results do not agree, #1 always yields a higher result. Use of the vapor pressure measured in #2 merely sets a lower limit on the calculated value of $S_{\text{critical}}$.

The following comments are to be noted about these runs:

1. The purification system was the same as that used in the earlier experiments (Line #1) for runs 19A to 29A except that a new cotton filter was inserted into the line before Run #19A as well as the new saturator, and the cotton filter was again replaced before Run #28A. Run #32A used line IX (Figure 23) as the purification scheme and Runs #33A and #35A used line IV (Figure 17).

2. A new calibration was carried out for runs #33A and 35A due to the long lapse of time between these runs and the previous calibration. A DC amplifier was added* in an attempt to increase the sharpness of

* Designed and built by C. Aker. Schematic is shown in Figure 24.
<table>
<thead>
<tr>
<th>Run #</th>
<th>T(_1)⁰K</th>
<th>Saturator Bath Temperature in °C</th>
<th>Flushing Time and Rate</th>
<th>Measured Vapor Pressure in mm.</th>
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<td></td>
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<td>10 hrs</td>
<td>-</td>
</tr>
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<td></td>
<td></td>
<td>1 lit/min</td>
<td></td>
</tr>
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<td>25A</td>
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<td>( T_2^{0K} )</td>
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<td>6.13</td>
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<td>259.3</td>
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</table>
DIRECT COUPLED AMPLIFIER

FIGURE 24
3. In Run #24, the photomultiplier tube was a 931A.
4. Both in Run #21A and #33A, two breaks appear on the oscillograph.

The first break is interpreted as due to an extraneous nucleus being activated, the resulting droplets falling into the region of observation. There is steady and very slight scattering for about 1/25 of a second before the main scattering starts. This second break is interpreted as the phenomenon of interest. This whole process may be analogous to the "double cloud" seen in the test chamber (see section 7b).

The amount of water vapor removed by these extraneous nuclei is not known. The supersaturation has been computed as if none were removed. The values of S at the second "break" are probably a little too high.

The results are definitely not in agreement with the Volmer-Flood data but rather they seem to divide into two classes, one near the Wilson cloud limit and the other somewhat lower (Figure 29).

c. The Volmer-Type Measurements

In order to check the reliability of the photoelectric technique, measurements were carried out using the classical technique: the gas and vapor are led into the chamber (which is flushed free of nuclei), the initial pressure (atmospheric)
and temperature noted and the expansion carried out. Observation was, visual, the observer looking into the chamber (at right angles to the light beam) through the glass rings (R). The final pressure in the chamber, at the initial temperature, was recorded and the ratio \( r_e = \frac{P_1}{P_2} = \frac{V_2}{V_1} \) obtained.

The field strength in all of these runs was 90 volts/cm rather than 60 volts/cm, since there should be no dependence on field strength for truly spontaneous nucleation.

To simplify the experimental procedure, the saturator was thermostatted to \( \pm 0.01^\circ C \) (by a Magneto-Set Thermoregulator with a Sargent Zero-Current relay) and the flow fixed at 3/4 liter per minute. The bath temperature (21.30\(^\circ C\)) was monitored with a Beckman thermometer. This procedure yielded a constant vapor pressure of 17.8 \( \pm 0.05 \) mm (saturation would yield 18.94 mm).

The purification system used was Line XI (Figure 18).

The modified light source (microscope lamp) was used in these measurements.

The results are given in Table 12 and graphically illustrated in Figure 25. From this figure, it is clear that the minimum value of \( S \) above which condensation was unequivocally observed was 7.7 at 258.1\(^\circ K\). The range appears to be \( S_{critical} = 7.3 - 7.7 \) at a temperature of 258.6 - 258.1\(^\circ K\).

This result coincides exactly with the higher set of values obtained photoelectrically. (See Figure 29).
<table>
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<tr>
<th>Test #</th>
<th>$T_1^\circ K$</th>
<th>$r_e$</th>
<th>$T_2^\circ K$</th>
<th>Saturator Bath Temperature $^\circ C$</th>
<th>Flushing Time &amp; Rate</th>
<th>$S_{\text{Terminal}}$</th>
<th>Comment</th>
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<td>7.06</td>
<td>Few par-</td>
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</tr>
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<td>7.60</td>
<td>Single drop-</td>
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<td></td>
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<td>$r_e$</td>
<td>$T_2^\circ K$</td>
<td>Saturator Bath Temperature °C</td>
<td>Flushing Time &amp; Rate</td>
<td>$S_{Terminal}$</td>
<td>Comment</td>
</tr>
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<td>--------------</td>
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<td>----------------------</td>
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<td>1.425</td>
<td>258.6</td>
<td>2.925</td>
<td>6 hrs 30.0 cm</td>
<td>7.30</td>
<td>Few particles***</td>
</tr>
<tr>
<td>32</td>
<td>297.5</td>
<td>1.375</td>
<td>261.7</td>
<td>2.93</td>
<td>2 hrs 29.0 cm</td>
<td>6.04</td>
<td>No cloud</td>
</tr>
<tr>
<td>33</td>
<td>298.4</td>
<td>1.428</td>
<td>258.5</td>
<td>2.86</td>
<td>3 hrs 29.5 cm</td>
<td>7.34</td>
<td>Cloud after long lag.</td>
</tr>
<tr>
<td>34</td>
<td>296.6</td>
<td>1.419</td>
<td>257.7</td>
<td>2.86</td>
<td>4 hrs 30.0 cm</td>
<td>7.90</td>
<td>Cloud</td>
</tr>
<tr>
<td>35</td>
<td>297.0</td>
<td>1.424</td>
<td>257.6</td>
<td>2.87</td>
<td>13 hrs 28.5 cm</td>
<td>7.98</td>
<td>Cloud</td>
</tr>
<tr>
<td>36</td>
<td>296.6</td>
<td>1.420</td>
<td>257.5</td>
<td>2.86</td>
<td>4 hrs 26.5 cm</td>
<td>7.29</td>
<td>Cloud</td>
</tr>
<tr>
<td>37</td>
<td>297.1</td>
<td>1.431</td>
<td>257.1</td>
<td>2.856</td>
<td>2 hrs 28.3 cm</td>
<td>8.21</td>
<td>Cloud</td>
</tr>
<tr>
<td>38</td>
<td>297.5</td>
<td>1.425</td>
<td>258.0</td>
<td>2.85</td>
<td>6.5 hrs 28.5 cm</td>
<td>7.69</td>
<td>Cloud</td>
</tr>
<tr>
<td>39</td>
<td>296.8</td>
<td>1.409</td>
<td>258.4</td>
<td>2.855</td>
<td>10 hrs 30.0 cm</td>
<td>7.55</td>
<td>Cloud— not dense</td>
</tr>
</tbody>
</table>

* A new section of CuO was moved into the oven.

** Ovens off before run.

*** Introduced new CuO charge
<table>
<thead>
<tr>
<th>Test #</th>
<th>$T_1,^\circ K$</th>
<th>$r_e$</th>
<th>$T_2,^\circ K$</th>
<th>Saturator Bath Temperature $^\circ C$</th>
<th>Flushing Time &amp; Rate</th>
<th>Terminal Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>297.4</td>
<td>1.413</td>
<td>258.7</td>
<td>2.865</td>
<td>2 hrs, 27.5 cm</td>
<td>7.26</td>
</tr>
<tr>
<td>29 July 52</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Few particles after long lag</td>
</tr>
<tr>
<td>41</td>
<td>298.0</td>
<td>1.410</td>
<td>259.5</td>
<td>2.90</td>
<td>8.5 hrs, 29.5 cm</td>
<td>6.94</td>
</tr>
<tr>
<td>31 July 52</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>No cloud</td>
</tr>
<tr>
<td>42</td>
<td>297.0</td>
<td>1.411</td>
<td>258.5</td>
<td>2.86</td>
<td>9.5 hrs, 29.5 cm</td>
<td>7.45</td>
</tr>
<tr>
<td>31 July 52</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>No cloud</td>
</tr>
<tr>
<td>43</td>
<td>297.4</td>
<td>1.419</td>
<td>258.2</td>
<td>2.853</td>
<td>11.5 hrs, 28.5 cm</td>
<td>7.60</td>
</tr>
<tr>
<td>31 July 52</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Few particles after long lag</td>
</tr>
<tr>
<td>44</td>
<td>297.0</td>
<td>1.418</td>
<td>258.0</td>
<td>2.93</td>
<td>6 hrs, 27.5 cm</td>
<td>7.74</td>
</tr>
<tr>
<td>1 Aug 52</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cloud</td>
</tr>
<tr>
<td>45</td>
<td>298.4</td>
<td>1.424</td>
<td>258.8</td>
<td>2.86</td>
<td>7 hrs, 28.5 cm</td>
<td>7.21</td>
</tr>
<tr>
<td>1 Aug 52</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Definite cloud!</td>
</tr>
</tbody>
</table>
Figure 25

- Points: Volmer type measurements
- Circle: Definite condensation
- Triangle: Few particles, long lag
- Triangle with No Field: No condensation

Temperature range: 256 °K to 260 °K

S values range from 7.0 to 8.5
d. Foreign Nucleation Studies

The last set of measurements was designed to test the validity of the adiabatic assumption by examining a situation in which the supersaturation at the condensation point is known. For unfiltered air, with nuclei which do not support supersaturation, $S_{\text{critical}} = 1$. If the initial vapor pressure of water is known, the value of $S_{\text{critical}}$, assuming the adiabatic law, can be computed.

To insure a plentiful supply of nuclei NaCl smoke was introduced into the chamber in all but the first two runs. This introduced other complications which will be discussed below.

The analysis flasks were placed so that the vapor pressure of the gas entering the chamber and that of the exit gas were measured. This technique is superior to the previous one of placing them in series at an exit port as the vapor pressure limits are more clearly defined. The arrangement is shown in Figure 26.

To allow an appreciable descent of the piston to occur before condensation (to overcome the lag of the mercury switch) a single 1 liter flask was used as the saturator resulting in a low partial pressure of water.

Run #T1 used an 18 liter carboy (half filled with an ice-water slush) as the saturator and the analysis flasks were in series at an exit port. Run #T9 used the 1 liter flask saturator but also used analysis flasks in series. The
LINE FOR TEMPERATURE MEASUREMENT

FIGURE 26
regular projection lamp provided the light source. Later experiments (T16 to T23) used the microscope lamp assembly.

For runs T16 to T23, the NaCl nuclei, generated from a hot Pt wire, were passed directly into the chamber. The total number of nuclei was varied by varying the time that the generator was on at red heat (after a 10 second warm-up). Then, the nuclei were flushed into the chamber for one minute. The chamber was sealed and the expansion carried out.

The photographic results are given in Figure 27 and 28 and the data is analysed in Table 13.

The results divide into two classes:

1. Without NaCl, using unfiltered compressed air and where very little NaCl was present, giving rise to two "breaks",

   \[ S \approx 1 \text{ (for the second "break")} \]

2. When appreciable quantities of NaCl were present or for the first "break" when small amounts of NaCl were present

   \[ S \approx .75 - .90 \]

10. Discussion of the Experimental Technique

The fundamental assumptions of the experimental technique are the following:

1. The growth of nuclei to visible droplets occurs rapidly enough so that the piston does not move an appreciable distance in the period from nucleation to the appearance of scattering.

2. The process is adiabatic.
<table>
<thead>
<tr>
<th>Run #</th>
<th>T&lt;sub&gt;1&lt;/sub&gt;</th>
<th>Carrier Gas; Impurity</th>
<th>Measured Vapor Pressure</th>
<th>Number of Pulses</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;4&lt;/sub&gt;</td>
<td>297.3</td>
<td>Compressed Air; Atmos.</td>
<td>#1 5.80; #2 4.32</td>
<td>3.82</td>
</tr>
<tr>
<td>T&lt;sub&gt;9&lt;/sub&gt;</td>
<td></td>
<td>&quot;</td>
<td>#1 .92; #2 3.35</td>
<td>5</td>
</tr>
<tr>
<td>T&lt;sub&gt;16&lt;/sub&gt;</td>
<td>296.6</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;; large am't NaCl</td>
<td>3.0</td>
<td>3.66</td>
</tr>
<tr>
<td>T&lt;sub&gt;17&lt;/sub&gt;</td>
<td>298.2</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;; unknown am't NaCl</td>
<td>4.03 ±.03</td>
<td>5.71</td>
</tr>
<tr>
<td>T&lt;sub&gt;18&lt;/sub&gt;</td>
<td>297.9</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;; very little NaCl</td>
<td>4.09 ±.03</td>
<td>9</td>
</tr>
<tr>
<td>T&lt;sub&gt;19&lt;/sub&gt;&lt;sub&gt;1&lt;/sub&gt;</td>
<td>296.7</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;; NaCl generated for 45 sec</td>
<td>3.97</td>
<td>6.57</td>
</tr>
<tr>
<td>T&lt;sub&gt;19&lt;/sub&gt;&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3.97</td>
<td>9.43</td>
</tr>
<tr>
<td>T&lt;sub&gt;20&lt;/sub&gt;</td>
<td>300.2</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;; NaCl on for 78 sec</td>
<td>4.32</td>
<td>7.43</td>
</tr>
<tr>
<td>T&lt;sub&gt;21&lt;/sub&gt;</td>
<td>296.1</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;; NaCl on for 111 sec</td>
<td>3.98 ±.02</td>
<td>5.67</td>
</tr>
<tr>
<td>T&lt;sub&gt;22&lt;/sub&gt;</td>
<td>296.2</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;; NaCl on for 144 sec</td>
<td>4.5 ±1</td>
<td>5.57</td>
</tr>
<tr>
<td>T&lt;sub&gt;23&lt;/sub&gt;&lt;sub&gt;1&lt;/sub&gt;</td>
<td>296.2</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;; NaCl generated for 31 sec</td>
<td>3.45</td>
<td>7.57</td>
</tr>
<tr>
<td>T&lt;sub&gt;23&lt;/sub&gt;&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3.45</td>
<td>10</td>
</tr>
<tr>
<td>Distance (cm)</td>
<td>r&lt;sub&gt;crit&lt;/sub&gt;</td>
<td>T&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Vapor Pressure at T&lt;sub&gt;2&lt;/sub&gt; at Cond.</td>
<td>S&lt;sub&gt;crit&lt;/sub&gt;</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------</td>
<td>-------------</td>
<td>----------------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>4.345</td>
<td>1.290</td>
<td>267.9</td>
<td>3.10 3.09</td>
<td>1.0</td>
</tr>
<tr>
<td>5.15</td>
<td>1.340</td>
<td>264.1</td>
<td>2.31 2.22</td>
<td>.97</td>
</tr>
<tr>
<td>4.55</td>
<td>1.305</td>
<td>266.4</td>
<td>2.76 2.06</td>
<td>.75</td>
</tr>
<tr>
<td>4.03</td>
<td>1.271</td>
<td>270.8</td>
<td>3.84 2.87</td>
<td>.75</td>
</tr>
<tr>
<td>4.90</td>
<td>1.328</td>
<td>265.8</td>
<td>2.63 2.75</td>
<td>1.05</td>
</tr>
<tr>
<td>4.01</td>
<td>1.266</td>
<td>269.8</td>
<td>3.57 2.85</td>
<td>.81</td>
</tr>
<tr>
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<td>1.320</td>
<td>265.3</td>
<td>2.53 2.68</td>
<td>1.06</td>
</tr>
<tr>
<td>4.51</td>
<td>1.30</td>
<td>270.2</td>
<td>3.67 3.01</td>
<td>.82</td>
</tr>
<tr>
<td>3.80</td>
<td>1.254</td>
<td>270.3</td>
<td>3.73 3.01</td>
<td>.78</td>
</tr>
<tr>
<td>3.90</td>
<td>1.260</td>
<td>269.9</td>
<td>3.59 3.24</td>
<td>.90</td>
</tr>
<tr>
<td>4.54</td>
<td>1.304</td>
<td>266.1</td>
<td>2.69 2.37</td>
<td>.89</td>
</tr>
<tr>
<td>5.10</td>
<td>1.340</td>
<td>263.2</td>
<td>2.15 2.20</td>
<td>1.02</td>
</tr>
</tbody>
</table>
In an effort to assess the validity of these hypotheses, the Volmer-type measurements and the foreign nucleation studies were carried out.

In the Volmer-type measurements, the supersaturated state is maintained for some period while the nuclei are allowed to grow. This occurs at the end of the expansion. The results were in exact agreement with those obtained with the photoelectric method for the higher critical supersaturation ratio indicating no appreciable growth time was involved. Moreover, the absence of the strobe pulses (which are quite rich in ultraviolet radiation) did not affect the upper limit. The glass effectively cuts off the undesirable radiation from the chamber.

The studies with foreign nuclei revealed the interesting behavior noted previously. The explanation of the observations is clear. It has been reported that NaCl particles, when exposed to a relative humidity of 78% or above, \((S > 0.78)\), grow rapidly into large droplets \((51b)\). Thus, when there is a high concentration of NaCl present, the condensation occurs at \(S = 0.75\) to 0.90. When ordinary unfiltered air is used, \(S_{\text{critical}}\) is 0.97 and 1.00 as would be expected if the adiabatic law held and the particles supported no supersaturation.

When small amounts of NaCl are present, in unfiltered \(N_2\), two "breaks" are observed. The first, small and steady, represents NaCl nucleation at \(S \approx 0.75\) while the second represents the much greater number of ordinary nuclei acting
at $S \approx 1.0$. Since we do not know how much vapor is removed by the NaCl in this case, the values of $S_{\text{critical}}$ for the second "break" are maximum values. From the very slight scattering at the first "break", there is probably not too much removed. With large quantities of NaCl enough is removed to prevent any further nucleation. It would seem that the adiabatic hypothesis is valid for this system (barring any accidental compensation of errors).

The error in $S$ due to errors in the measurement of $T$, $p_1$ and $r_e$ may be estimated according to the scheme outlined in section 8.

The probable error in $T_1$ is small, amounting at most to $\pm 0.2^\circ$; the resulting error in $S$ is negligible ($\sim 2\%$) while the error in $T_2$ is about $0.2^\circ$ ($\sim 1\%$).

The error in $r_e$ may be estimated in the following manner: the strobe pulses appear in the piston photograph with a spacing of approximately $0.25$ cm. The determination of the location of the oscillograph "break" is definitely within one-half a pulse interval and hence the piston distance is in error by no more than $\sim 0.13$ cm. Since $r_e$ is of the form

$$r_e = 1 + \frac{.9h}{13}$$

then

$$|\Delta r_e| \leq (\frac{.9\sqrt{3}}{13})|\Delta h|$$

When $|\Delta h| \leq 0.13$ cm, $|\Delta r_e| \leq 0.01$. This leads to an error in the computed value of $S_{\text{critical}}$ of about $7\%$; the error in $T_2$ is about $0.8^\circ$ ($\sim 3\%$).

The total error in $S_{\text{critical}}$ due to errors in $T_1$ and
\( r_e \) is then only about 10%; the error in \( T_2 \) is large, amounting to \( 1.9^\circ \). Note that the errors in \( T_1 \) and \( r_e \) affect both \( S \) and \( T_2 \).

Errors in \( p_1 \), which alter only \( S_{\text{critical}} \), are not as easily computed. For the early runs, 1A - 14A, where no measurement was made, it is not likely that the error in \( p_1 \) is greater than \( \pm 1 \) mm, which implies \( \sim 20\% \) error in \( S_{\text{critical}} \). To illustrate the reason for this, the vapor pressure necessary so that at the computed final temperature, the results would coincide exactly with the results of Pound (for nucleation on ions) has been calculated (Table 14). It is clear that the errors in assumed vapor pressure need not be too large to allow the measurements to give exact agreement.

For the later runs, where measurements of the vapor pressure were made, the errors can be assessed a little more adequately. In particular, the measurements indicate that with the larger saturator, significant variations from saturation are observed indicating that the assumed values for the vapor pressure in the earlier work may be too high (at the high bath temperatures in any event). This agrees with the calculation shown in Table 14.

In runs 19A to 36A, the error is probably not more than 1 mm, or about 10\% in \( S_{\text{critical}} \).

In the Volmer-type measurements, the error due to uncertainty in \( p_1 \) is probably not more than 0.1 mm, a negligible error in \( S_{\text{critical}} \). (The error in \( r_e = \sim 0.002 \).)
**TABLE 14**

Estimated Vapor Pressure Errors

<table>
<thead>
<tr>
<th>Run #</th>
<th>Assumed Pressure</th>
<th>Pressure Error*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>15.0 mm</td>
<td>+0.5mm</td>
</tr>
<tr>
<td>3A</td>
<td>14.5</td>
<td>+4.0</td>
</tr>
<tr>
<td>4A</td>
<td>14.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5A</td>
<td>14.6</td>
<td>+2.6</td>
</tr>
<tr>
<td>9A</td>
<td>15.5</td>
<td>+1.5</td>
</tr>
<tr>
<td>10A</td>
<td>15.2</td>
<td>+1.7</td>
</tr>
<tr>
<td>11A</td>
<td>7.5</td>
<td>+0.4</td>
</tr>
<tr>
<td>12A</td>
<td>7.0</td>
<td>0.0</td>
</tr>
<tr>
<td>13A</td>
<td>4.6</td>
<td>-0.9</td>
</tr>
<tr>
<td>14A</td>
<td>4.5</td>
<td>-0.5</td>
</tr>
</tbody>
</table>

*The error is estimated by subtracting the assumed vapor pressure from the pressure computed to cause the experimental data to agree with that of Pound.*
The foreign nucleation studies seem to indicate a fairly consistent saturation, with an error no greater than 0.5 mm, with a resulting error in $S_{\text{critical}}$ of about 10%.

In summary:

<table>
<thead>
<tr>
<th>Runs</th>
<th>Total Error in $S_{\text{critical}}$</th>
<th>Error in $T_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A - 14A</td>
<td>$\sim 30%$</td>
<td>$\pm 1^o$</td>
</tr>
<tr>
<td>19A - 34A</td>
<td>$\sim 20%$</td>
<td>$\pm 1^o$</td>
</tr>
<tr>
<td>Volmer-type</td>
<td>$\sim 5%$</td>
<td>$\pm 5^o$</td>
</tr>
<tr>
<td>measurements</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T1 - T 23</td>
<td>$\sim 20%$</td>
<td>$\pm 1^o$</td>
</tr>
</tbody>
</table>

These are maximum errors. The actual location of the "break", which determines $r_3$, is probably better than one-half a pulse interval; the error in $p_1$ is also very likely smaller.

11. Discussion of Results

Since this research was initiated there have been two other reported investigations of the spontaneous nucleation of water vapor.

Pound (33), using an apparatus very similar to that of Sander and Damköhler, has carried out an extensive series of measurements in various carrier gases over a very wide temperature range. The results at the higher temperatures (in which our own work was performed) are summarized below. (See Figure 29).

1. The critical supersaturation ratio for condensation in the absence of an electric field, using air, $O_2$ and $N_2$ as carrier gases, is virtually identical with the Volmer-Flood results for the similar situation.
2. In the presence of an electric field the critical limit obtained in O₂ and air is virtually the same as that found by Volmer and Flood.*

3. For N₂, there is a distinct and appreciable elevation of the critical supersaturation ratio in the presence of an electric field.

4. Very recently (59c), using H₂ as a carrier gas, in the presence of an electric field, the results for water vapor were found to be virtually those found by Wilson and Powell.

This last result is very striking.

Pound at first interpreted these results as due to the variable content of ions in the various carrier gases, increasing from H₂ through N₂ being highest in O₂. Wilson and Andren expressed similar views to account for the anomalous behavior of H₂ (in which no ion limit could be found). In a more recent report (59d), Pound considers either that the characteristics of the energy transfer in H₂ are sufficiently different to effect the change or that the presence of permanent dipoles in the other gases heterogeneously nucleate the water vapor. He does not elaborate on these arguments.

Pollerman (58) and Rathje and Stranski (65) using a

* A very early report (59b) failed to confirm the Volmer-Flood data with air but insertion of an extra three foot section of cotton filter into the purification system raised the observed critical supersaturation ratios to those observed by Volmer and Flood. This is a striking illustration of the need to examine results carefully.
chamber devised by Pollerman (Figure 1h) have reported confirmation of the Volmer theory for spontaneous nucleation and for condensation on negative ions (though for ions the situation is somewhat uncertain as one experimental point must be used to correlate the theory with the other experimental points). The results are shown in Figure 3a.

The situation has clearly not been settled by either of these investigators though the work of Pound (and essentially Wilson and Andren) sheds light on the situation.

The results obtained in this research may be classified as follows:

1. Without an electric field, the critical supersaturation ratios for H₂O (in N₂) appear to agree with the earlier results for nucleation on ions.

2. In the presence of an electric field, the results seem to divide randomly into two groups. The lower group of critical supersaturation ratios centers around the results obtained by Pound using N₂ while the higher group centers around the Wilson cloud limit, obtained by Pound using H₂.

3. The Volmer-type measurements yield the higher value (though they were carried out at a higher field strength than the photoelectric measurements). An interesting point is that not once at these high supersaturations were the very dense clouds observed which are described by earlier investigators.
VOLMER & FLOOD, FIELD, AIR (CURVE — T)

POUND, FIELD, N₂ (CURVE ———)

SALTSBURG & REISS, FIELD, N₂

ANDERSON & FROEMKE, CLOUD LIMIT, AIR

POWELL, CLOUD LIMIT, AIR

WILSON, " " ""

SANDER & DAMKOHLER, FIELD, AIR

POWELL, RAIN LIMIT, AIR

WILSON, POSITIVE ION LIMIT, AIR

SANDER & DAMKOHLER, NO FIELD, AIR

POUND, NO FIELD, N₂

THEORETICAL

CRITICAL SUPERSATURATION RATIOS OF H₂O

FIGURE 29
The experimental facts which must be correlated are the following:

1. The existence of nuclei effective in the range 1.25 \( \leq r_e \leq 1.38 \) which are few but nearly constant in number, which do not exist in freshly prepared hydrogen, and which are not affected by a field of 400 volts/cm (in air) (Wilson and Andren).

2. The data of Volmer and Flood indicating that spontaneous nucleation occurs below the positive ion limit set by Wilson.

3. Assuming Andren's data are correct, the failure of the number of observed droplets to change very sharply with supersaturation in the region denoted by Volmer and Flood for the occurrence of spontaneous nucleation as would be predicted by theory.

4. The dependence of the number of observed droplets, in the presence of the same electric field, upon the intensity of the ionizing source (Andren).

5. The internal consistency of any given set of data.

6. The influence of the various carrier gases (\( O_2, N_2, H_2, \) air) on the process (Pound, Wilson).

7. The results of this research indicating that either result obtained by Pound (in \( N_2 \) or \( H_2 \)) can be obtained using \( N_2 \) alone.

8. The almost universal agreement on the data for the (negative) ion limit.
9. The role of reevaporation nuclei.

It must be clearly recognized that a major part of the disagreement lies in the specific criterion of condensation taken by various investigators. Whether 1 droplet/cc or "definite cloud" is used to define condensation actually seems to make a difference. Theory indicates that such should not be the case; calculations for water vapor indicate a 20% difference in $S_{critical}$ for a difference in $I^*$ of $10^6$. Clearly, this range must include all criteria employed yet the experimental discrepancies are much greater ($\sim 60-70\%$).

The 1:1 correspondence between nuclei formed and droplets observed has been tacitly assumed. There have been two numerical investigations of this problem, based upon quite different concepts. Barnard (5) has considered the problem as one in which the actual integral of $I^*$ over time must be computed where the time dependent parameter is the terminal temperature reached by the expanded gas. For this function, the analysis of Williams (81) was employed. The author obtained as a typical result for water

$$N_0 = 10^{-2} I_0 \left(\frac{V}{S}\right)^2$$

where $I_0$ is the initial rate of drop formation, $N_0$ is the number of droplets observed.

Further corrections were introduced to take account of the finite time of expansion and the probable failure to attain the theoretical (adiabatic) terminal temperature. The value of $N_0$ then appears to be somewhat lower. It does not...
account for the 60% experimental discrepancy.

Mason (5la) has attempted to show by calculation how the data of Frey may be explained. He considers the expansion to proceed stepwise, at each step (in ΔV) taking account of the vapor removed and the heat of condensation liberated. The calculation, however, involves a knowledge of the rate of growth of nuclei - a difficult approximation to evaluate. The agreement is only qualitative and sheds little light on the situation.

There is no criterion which is clearly valid. Any discussions of the various criteria can be meaningful only when a decision as to the spontaneity of the process can be made. The presence of impurity renders any definition or criterion of condensation quite useless.

The correlation of most of these results is possible on the basis of the following hypothesis: the discordant experimental findings result not from the inherently ionized nature of the carrier gas alone but from the efficiency with which any given piece of apparatus is able to remove ions from the chamber.

Ions are continuously being formed in any piece of apparatus even when a field is applied. As pointed out earlier, in most chambers (except those of Sander and Damköhler, Pound, and the chamber used in this research) where a clearing field is used, field-free spaces exist inside the chamber with the consequent possibility of ions entering the region of obser-
The average number of ions per cc formed in field-free space is large (~10^3) compared to the number existing in the region of the field. Hence, relatively large numbers may be pulled into this region. If these ions are not all removed, spurious results will be obtained.

The observation by Andren on the influence of various field strengths on artificially and naturally ionized air is striking evidence for the failure of a strong field of this type to remove all the ions present.

If this is true, the results become meaningful. The inability of Wilson to affect the number density in the range 1.25 ≤ r_e ≤ 1.38 is simply due to the small but constant number of ions which were not removed by the field. There is no need to postulate the production of ions by the expansion.

The internal consistency of any set of data is due to the constant average behavior of the apparatus in yielding ions.

The failure of the nucleation frequency to rise sharply with almost 70% change in supersaturation, as indicated by Andren and Wilson in the range 1.25 ≤ r_e ≤ 1.38, is in sharp contrast with the predictions of the theory of spontaneous nucleation. It does occur at the Wilson limit (where no attempt was made to remove ions).

The Volmer-Flood results probably represent hetero-

* See section 3.
geneous nucleation on ions* since they fall below the positive ion limit (and below the cloud limit) but above the negative ion limit. The data of Frey, in which artificial ionization was used to purify the gas, may be extrapolated to yield the Volmer-Flood data.

The variation in behavior due to carrier gas and the "anomolous" behavior of H₂ can be explained as due to the varying numbers of ions in the H₂, O₂, and N₂ as Pound originally suggested. In chambers in which clearing of ions is inefficient, the gas with the lowest ion content will yield the highest value of $S_{\text{critical}}$ (for a given criterion). When the clearing field is efficient, it makes no difference.**

The very inhomogeneous field used by Pound may not be efficient.

The failure to observe the very dense clouds at or near the cloud limit in this research cannot be explained unless it is assumed that the field was not fully efficient and that the true spontaneous limit had not yet been reached.

The sporadic occurrence of values around the positive ion limit may be due to the random occurrence of ionic impurity. The Volmer-type measurements at the higher field strength yielded the higher ratio; random occurrence of lower effective ratios would not be observed due to the short range of supersaturation studied.

* This has been suggested by Pound.

** Crude theory shows that $S_{\text{critical}}$ should decrease with increasing ion content (76a).
For the reasons given above, the decision as to which condensation criterion is valid becomes somewhat obscure and vague.

One can only say that the Becker-Doring theory in the present quantitative form (including the use of $I^* = 1$ as the condensation criterion) is not correct. There are many sources of error, some of which have been mentioned; others will be mentioned in the following chapter.

One interesting point may be noted: the growth of the particles is certainly not instantaneous (on a time scale of 1/50 second observational intervals) as judged from the oscillographs. That this is not an artifact of the electronics (high frequency cutoff) is clear else the strobe pulses would not have passed undistorted. It may even be possible to obtain information on the growth law since the intensity follows a law like (80)

$$I = K n r^\gamma$$

$I =$ intensity of scattered light  
$n =$ number density of particles  
$r =$ mean radius  
$\gamma =$ coefficient depending upon relative value of $r$ and wavelength of light  
$K =$ constant

though this would have to be examined carefully.

12. Suggestions for Further Work

The lack of a reliable purification system is clearly a definite deficiency for spontaneous nucleation studies and even for foreign nucleation studies with specific nuclei. Until such a system is produced and a method of establishing
purity found, studies such as these will always be subject to question.

The chamber described previously can be improved in several ways and these will be outlined before describing the suggested plan of attack on the nucleation problem.

1. The observation of scattering should not be made at 90° but at some forward angle where the scattering is more intense for smaller particles (83c).

2. The light source should be modulated to simplify the electronic components (permitting AC amplifiers to be used) and allowing noise reduction to be more easily carried out.

3. In order to see more of the beam, the observing lens of the phototube should be a wide angle lens. This will also provide a more intense signal.

4. The minimum size and concentration of particles detectable by the optical setup should be determined by calibration with homogeneous aerosols.

5. The descent of the piston may be followed electrically by placing a resistance wire on the side of the piston and calibrating the resistance of the wire (due to that portion above the Hg) against expansion ratio. The initial position can then be fixed electrically. A function of this resistance may then be displayed on the oscillograph on one axis (say the y axis) while the phototube output is displayed on the x axis. The
Hg switch will also be eliminated as the sweep can be set to trigger at a given resistance.

6. Alternatively the piston roof and Hg surface may be caused to act as plates of a capacitor and the variable capacity related to piston height.

Once the chamber is in good operating condition the hypothesis outlined above is capable of experimental test. It merely involves placing electrodes inside the chamber in various positions and using various field strengths. If the hypothesis is correct, electrode systems such as shown below should not allow the attainment of the high supersaturations previously obtained.

The testing of various carrier gases, with these modifications, should prove of great interest. In particular, the results with H₂ should be the same irrespective of the electrode scheme while those with N₂ should definitely depend upon the location of the electrodes and the field strength.
IV. THE THEORY OF NUCLEATION

1. Introduction

It has been pointed out that the experimental observation represents an integrated process of nucleation followed by growth. To facilitate the theoretical development, these processes must be separated. The usual assumption asserts that the nuclei grow instantaneously to visible droplets and, consequently, the theory has centered about the calculation of the rate of development of nuclei which are capable of growth.

In the following sections, the relevant thermodynamic background will be reviewed and the theory will be presented in its most refined mathematical form, that due to Frenkel (22b). This will be followed by a detailed analysis in which the conceptual weaknesses of the theory will be reviewed as well as a new analysis of the fundamental thermodynamic postulate.

Various other proposals to modify the theory will be examined.

2. Thermodynamics of Surfaces

The usual treatment of systems in which a new state variable is to be considered consists in the inclusion in the fundamental equation of the relevant variable in the form of its work term. For systems involving non-homogeneous interfaces, this is not a valid procedure when the details of the interface are relevant, since the usual equations are developed for strictly homogeneous phases with geometrically sharp boundaries. However, a device, due to Gibbs (27a) en-
ables one to treat such systems.

Consider a two phase system, separated by some non-homogeneous interface. Let there be passed through the non-homogeneous region a dividing surface* "similarly situated with respect to the condition of adjacent matter" (27a). Consider the matter on either side of the d.s. to be homogeneous right up to the d.s. The interface characterized by the d.s. can now be defined precisely by its geometrical parameters, the surface area, \( A \), and the principal radii of curvature, \( C_1 \) and \( C_2 \).

Gibbs then writes for the total internal energy, \( U_T \), (27e)

\[
U_T = U_1(S_1, V_1, N_1) + U_2(S_2, V_2, N_2) + U_S(S_s, N_s, A, C_1, C_2) \tag{4.1}
\]

where \( U_1, U_2 \) = energy of phase 1 and 2 assuming them homogeneous right up to the d.s.

\( U_S \) = a correction term which may be positive or negative and to which is assigned the dependence of energy on \( A, C_1, C_2 \) as well as the correction terms \( S_s, N_s \).

Equation (4.1) essentially defines \( U_S \); other extensive quantities, \( S_s \) and \( N_s \), are similarly defined.

In differential form, the fundamental equation may be written (27f)

\[
dU_T = TdS_T - P_1dV_1 - P_2dV_2 + \mu dN_T + s dA + \Theta_1 dC_1 + \Theta_2 dC_2 \tag{4.2}
\]

where the equilibrium conditions (27g)

\[
T_1 = T_2 = T_S \quad ; \quad \mu_1 = \mu_2 = \mu_S \tag{4.3}
\]

have been used.

* Denoted in the following by d.s.
From this relation, the further condition of equilibrium

$$P_2 - P_1 = \tau (C_1 + C_2) + \Theta_1 \frac{dc_1}{dV} + \Theta_2 \frac{dc_2}{dV}.$$  \hspace{1cm} (4.4)

is obtained.* It is essentially a generalized Kelvin relation (11).

Gibbs now chooses to locate the ds. (which up to now has had an arbitrary location) by choosing $\Theta_1 + \Theta_2 = 0$

and assuming $\Theta_1 - \Theta_2 = 0$ \hspace{1cm} (4.5)

(the latter condition being satisfied by a spherical interface).

The usual Kelvin relation results:

$$P_2 - P_1 = \tau (C_1 + C_2)$$ \hspace{1cm} (4.6)

$$= \frac{2\tau}{r}$$ \hspace{1cm} for spherical interfaces. (2.3)

This thermodynamic criterion of equilibrium for the particular surface defined by $\Theta_1 + \Theta_2 = 0$ is the same as the condition of mechanical equilibrium defined by the Kelvin law, and hence, the quantity $\tau$ may be identified with the mechanical macroscopic surface tension obtainable experimentally by application of the Kelvin law (or relations based upon similar considerations regarding the quantity $\tau$ as a mechanical parameter).

For this surface, known as the Surface of Tension, the work of formation of a spherical segment of the new phase is $(1/3)\tau A$.

Thus,

$$\langle \Delta U \rangle_{\tau, N, V} = \text{Reversible Work of Formation} \ (4.7)$$

* This follows from $V_T = V_i + V_L$ and $(\delta U_T)_{\tau, N, V} = 0$. 


\[ U_{\text{Vapor}} = U' = T S_T + \mu N_T - P_1 (V_1 + V_2) \]  
\[ U_{\text{Vapor plus new phase}} = U'' = T S_T + \mu N_T - P_1 V_1 - P_2 V_2 + \sigma A \]

Therefore

\[ (\Delta U)_{S_T, N_T} = U'' - U' \]
\[ = -(P_1 - P_2) V_2 + \sigma A \]
\[ = \frac{\sigma A}{3} \text{ for a spherical segment} \]

If one considers the interface to be planar, the terms \( \Theta_1 \) and \( \Theta_2 \) do not appear and it is then possible to define another dividing surface. From the Gibbs-Duhem relation, for a one component system (271)

\[ d\Gamma = -S^s dT - \Gamma d\mu \quad \text{where} \quad S^s = S_s / A \]

If one sets \( \Gamma = 0 \) to define the surface (called the "\( \Gamma = 0 \)" surface),

\[ d\Gamma = -S^s dT \]
\[ d\Gamma / dT = -S^s \]

which is a form of the Gibbs adsorption equation. It is valid for other planar surfaces in addition to the \( \Gamma = 0 \) surface since \( \tau \) is rigorously independent of the location of the planar d.s. (27j).

The fundamental equation for the \( \Gamma = 0 \) surface takes the same form as Equation (4.2) except that

\[ N_T = N_1 + N_2 \]
\[ N_s \equiv 0 \]

This equation does not admit of an integrated form due to the presence of the intensive parameters \( c_1 \) and \( c_2 \) and hence a Gibbs-Duhem relation does not result from an application of Euler's Theorem.

3. The Frenkel Theory

The classical theory of nucleation, in the form developed
by Frenkel (22b) and Zeldowitch (84b) is based upon the concept of the heterophase fluctuation (22a). Frenkel considers that fluctuations in density in the vapor phase are sufficiently great as to lead to the formation of fragments of the liquid phase (spherical liquid droplets) and that an equilibrium distribution of these fragments exists in both the unsaturated and supersaturated vapor (within a certain range).

To illustrate the nature of this phenomenon, it is instructive to examine the equilibrium condition of a system composed of a single liquid droplet and a large mass of surrounding vapor. The most convenient procedure is to examine the relevant thermodynamic potential. In particular, the difference in thermodynamic potential between the system in which all the molecules are in the vapor state and that in which a given number have condensed to form a liquid droplet (the rest remaining in the vapor), subject to the proper constraints, yields the work of formation of such a droplet. The formulation as given by Frenkel will be presented here but it should be noted that it represents an approximation, the validity of which will later be examined (section 4).

The fundamental assumption of the Frenkel theory is the expression of the thermodynamic potential, $\bar{\Phi}$, of the system vapor plus droplet in the form

$$
\bar{\Phi} = N_1 \mu_1 (P, T) + N_2 \mu_2 (P, T) + 4\pi r^2 \sigma
$$

(4.16)

where

- $N_1$ = number of vapor molecules
- $N_2$ = number of molecules in the droplet
- $\mu_1$ = chemical potential per molecule in the vapor phase at pressure $P_1$
\( \mu_2 \) chemical potential per molecule in the liquid phase at pressure \( p \)
\( r \) = radius of the droplet
\( \gamma \) = bulk surface tension of the liquid

Frenkel assumes that the Gibbs free energy of the droplet can be expressed as the Gibbs free energy that the liquid molecules would have were they present at the pressure outside the droplet (since from the Kelvin law, the pressure inside the droplet is larger) plus a contribution from the surface to the free energy, of \( \sigma A \).

Since \( \Phi \) is identified with a Gibbs free energy, the condition of equilibrium is given by
\[
(\delta \Phi)_{T, P, N_T} = 0 \tag{4.17}
\]
from which may be derived
\[
\mu_1 (p, T) = \mu_2 (p, T) + \frac{2 \sigma V_2}{r^*} \tag{4.18}
\]
where \( r^* \) = the radius of the droplet in equilibrium with the vapor and \( V_2 \) = partial molecular volume of the liquid phase (assumed incompressible).

Further examination of the function \( \Phi \) reveals that the condition given by (4.17) leads to a maximum value of \( \Phi \) rather than a minimum and hence represents an unstable equilibrium.

To illustrate this more clearly, consider the reversible work of formation of the droplet:
\[
\Delta \Phi = (\Phi - \Phi_0)_{T, P, N_T} \tag{4.19}
\]
where \( \Phi_0 \) = Thermodynamic potential of vapor
\[
\Delta \Phi = (N_1 + N_2) \mu_1 (p, T) - N_1 \mu_1 (p, T) - N_2 \mu_2 (p, T) - 4 \pi r^2 \sigma \tag{4.20}
\]
\[
= (\mu_2 - \mu_1) N_2 + 4 \pi r^2 \sigma
\]
This is valid for any value of r. There is, however, only one value of r for which $\mu_2 - \mu_1$ is known (and for which $\sigma$ is defined) and that is given by equation (4.18). Substitution into equation (4.20) yields for $r = r^*$

$$
\Delta\Phi^* = 4\pi \sigma \left[ - \frac{2}{3} r^* \pi^2 + r^2 \right]
$$

in agreement with the value found previously from the exact analysis (Equation 4.12).

If one examines the behavior of $\Delta\Phi$ away from equilibrium, certain qualitatively useful features emerge. Thus, let the vapor be unsaturated, i.e. $\mu_2 > \mu_1$. The function $\Delta\Phi$ is then always positive and hence there is no possibility of ever spontaneously forming a droplet from the vapor. When the vapor is supersaturated, $\mu_1 > \mu_2$ and the function $\Delta\Phi$ passes through a maximum. To see this, insert (4.18) into (4.20) to obtain

$$
\Delta\Phi = 4\pi \sigma \left[ - \frac{2}{3} r^* \pi^2 + r^2 \right]
$$

This function passes through a maximum at $r = r^*$ (where $\Delta\Phi = \frac{1}{3} \sigma A$). This is illustrated in Figure 30 where $\Delta\Phi$ is sketched as a function of $r$. (Note that $\Delta\Phi$ is only really defined at $r = r^*$, an equilibrium point; anywhere else it is not thermodynamically definable as the system is not in equilibrium. Qualitatively though, it is useful to consider this dependence on $r$).

It is clear that for $r < r^*$, $\Delta\Phi$ is positive. Such droplets called embryos, cannot arise in a spontaneous fashion.
REVERSIBLE WORK OF FORMATION OF A NUCLEUS

FIGURE 30
When \( r > r^* \) the droplet can grow with a decrease in \( \Delta \Phi \), a possible spontaneous process. The point \( r = r^* \) represents a condition where the drop can either grow or decay spontaneously. The droplet of radius \( r = r^* \) is called a nucleus (or critical nucleus).

The connection with the supersaturation phenomenon is clear. By a fluctuation process, embryos arise and grow up to become nuclei. Once in this latter condition, further growth can proceed spontaneously. In a sense, the quantity \( (\Delta \Phi)_{r=r^*} \) is an "activation energy" for the spontaneous conversion of vapor to a droplet. It arises through the introduction of the quantity \( \gamma \), the surface tension, which is important when the dimensions of the phase are such that the surface contribution cannot be neglected. The rate of formation of nuclei represents, then, the rate determining step in the kinetic process of the transformation (by analogy with ordinary chemical kinetics).

Having briefly introduced the relevant concepts, the determination of the embryo distribution can now be carried out. According to the Fresnel Hypothesis, a spectrum of embryos exist in the vapor phase, arising through fluctuations. The analysis, however, accords to embryos of all sizes, equilibrium properties. The rationalization of this procedure is simply that only one size of droplet, the nucleus, is important and one never need know the actual distribution of embryos. In a sense, the analysis is really based upon the
fluctuation theory as proposed by Einstein.

To carry out this program, one assumes that the various sized embryos form an ideal dilute solution in the "solvent" of single vapor molecules, each embryo of a given size being one of the types of solute. (Spherical embryos are assumed).

Let \( n(x) \) be the number of embryos of a given size, \( x \), with a chemical potential \( \mu_x \) per embryo. If \( \mu_i \) is the chemical potential of the gas; per molecule, the thermodynamic potential of the system, \( \Phi \), may be written:

\[
\Phi = n_i \mu_i + \sum_x n(x) \mu_x + kT \left[ n_i \ln \frac{n_i}{F} + \sum_x n(x) \ln \frac{n(x)}{F} \right]
\]

(4.24)

where

\[
F = n_i + \sum_x n(x) \leq n_i
\]

(4.25)

(The last two terms in (4.24) arise explicitly when one chooses to regard \( \mu_i \) and \( \mu_x \) as functions of the total pressure, \( p_1 \)).

The equilibrium condition, Equation (4.17), coupled with the conservation condition

\[
\delta N_T = \delta N_1 + \sum_x \delta n(x) = 0
\]

(4.26)

leads to

\[
n(x) = F \exp \left( \frac{1}{kT} \left[ \mu_x - x \mu_i \right] \right)
\]

(4.27)

It has been noted that the Frenkel approximation regards \( \mu_x \) as composed of an intrinsic chemical potential the material would have if it existed at the pressure outside the droplet plus a surface term and hence

\[
\mu_x \equiv x \mu_2 (p_i, T) + 4 \pi \sigma \frac{2}{3}
\]

(4.28)

or in terms of the number of molecules, \( x \), since \( \frac{4 \pi \sigma^3}{3} = x \lambda \),

\[
\mu_x = x \mu_2 + \alpha x^{2/3}
\]

where \( \alpha = 4 \pi \sigma \left( \frac{2}{4 \pi \lambda^3} \right)^{2/3} \)

(4.29)
Equation (4.27) may then be written

\[ n(x) = n_1 \exp \left( -\frac{1}{\kappa T} \left[ x(\mu_2 - \mu_1) + \alpha x^{2/3} \right] \right) \]  

(4.30)

It is interesting to note the following facts:

1. For an unsaturated state \( \mu_2 > \mu_1 \) the quantity \( n(x) \) goes exponentially to zero as \( x \) increases. For a supersaturated state, \( n(x) \) goes through a minimum defined by

\[ \left[ \frac{d}{dx} \frac{d n(x)}{dx} \right]_{x=x^*} = 0 \]  

(4.31)

This leads directly to Equation (4.18)

\[ \mu_2 - \mu_1 = \frac{2}{3} \alpha x^{*\cdot1/3} = \frac{2 \sigma V_2}{R} \]

which relation defines what has been previously called the nucleus. The least probable embryo is the nucleus (85).

2. The exponent is equal to \( \sigma^A / 3 \) for the nucleus.

3. For the supersaturated vapor, one must not allow any arbitrary sized droplet to appear in the system (7b).

Thus,

\[ N_T = \sum_x x n(x) + N_1 = \text{constant} \]  

(4.32)

but \( \sum_x x n(x) \) diverges badly once the nucleus size \( x^* \) is passed and hence, to retain the validity of the expression for the conservation of the total number of particles, there must be a cutoff at or slightly beyond \( x^* \). This is essentially where growth is separated from nucleation and this internal constraint keeps the metastable state from collapsing! There is no convergence problem for an unsaturated vapor.

4. The expression for \( n(x) \) may be written in a form involving the measurable variables when \( \mu_2 - \mu_1 \) is expressed in terms of pressure and temperature.
For an ideal gas
\[ \mu_1(p_1, T) = \mu_1^0 + \kappa T \ln p_1 \quad (4.33) \]

For liquid-vapor equilibrium at the saturation pressure, \( p_\infty \),
\[ \mu_2(p_\infty, T) = \mu_1(p_\infty, T) \quad (4.34) \]

Since the liquid is nearly incompressible
\[ \mu_2(p_\infty, T) \approx \mu_2(p_1, T) \quad (4.35) \]

hence
\[ \mu_2 - \mu_1 = \kappa T \ln \frac{p_\infty}{p_1} = \frac{2\sigma \sqrt{\nu}}{\gamma} \quad (4.36) \]

combined with (4.30) yields
\[ n(x) = n_1 \exp -\frac{1}{kT} \left[ x \kappa T \ln \frac{p_\infty}{p_1} + \alpha x^{2/3} \right] \quad (4.37) \]

The quantity \( n(x^*) \) is given by
\[ n(x^*) = n_1 \exp -\frac{1}{kT} \left[ \frac{4\alpha^3}{27(\kappa T \ln p_\infty)^2} \right] \quad (4.38) \]

since \( x^* \) (defined by (4.31)) is given by
\[ x^* = \frac{8\alpha^3}{27(\kappa T \ln p_\infty)^3} \quad (4.39) \]

4. The Rate Theory

The quantity of interest is the rate of passage of embryos through the nuclear size in a given volume at a given pressure and temperature since (a) nuclei are capable of spontaneous growth and (b) the observed droplets have been assumed to arise in a 1:1 fashion from the nuclei. The treatment below is essentially that of Zeldowich though originally formulated and solved by Becker and Doring.

Let \( S_x \) be the surface area of an embryo of size \( x \), \( \alpha_x \) the probability per unit area that a molecule will evaporate from \( S_x \) in unit time. In the time \( dt \) then,
\[ S_x \alpha_x dt \]
is the probability that a single molecule will evaporate
from an embryo of size \( x \). If \( S_{x-1} \) is the surface area of an embryo of size \((x-1)\), \( \beta \) the number of impacts/second/unit area of single molecules on this embryo, then in the time \( dt \),

\[
S_{x-1} \beta dt
\]

will be the probability that a molecule will condense on the embryo of size \((x-1)\).

If \( f_{x,t} \) represents the number of embryos of size \( x \) at the time \( t \) (a non-equilibrium distribution), then the flux, \( I_x \), (in numbers of embryos passing through a given size, \( x \), per unit time) is given by

\[
I_x = f_{x-1,t} S_{x-1} \beta - f_{x,t} S_x \alpha_x
\]

(4.40)

One ignores all collisions between embryos: they grow and evaporate in steps of single molecules only. (This point will be considered in Chapter VI).

At equilibrium

\[
I_x = 0
\]

by detailed balancing

(4.41)

and

\[
f_{x,t} = \eta(x)
\]

the equilibrium distribution (4.42)

Hence

\[
\alpha_x = \frac{n_{x-1} S_{x-1} \beta}{n_x S_x}
\]

(4.43)

whence from (4.40) and (4.43) one obtains

\[
I_x = n_{x-1} S_{x-1} \beta \left[ \frac{f_{x-1,t}}{n_{x-1}} - \frac{f_{x,t}}{n_x} \right]
\]

(4.44)

If \( x \) is regarded as continuously variable, (4.44) becomes

\[
I(x) = -n(x) S(x) \beta \left[ \frac{\partial}{\partial x} \left( \frac{f(x,t)}{n(x)} \right) \right]
\]

(4.45)

and

\[
\frac{\partial f(x,t)}{\partial t} = - \frac{\partial I(x,t)}{\partial x}
\]

(4.46)

from the equation of continuity (when there are no sources or sinks in the system).
Combining (4.45) and (4.46) one obtains
\[
\frac{\partial f(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ n(x) \frac{\partial}{\partial x} \left( \frac{f(x,t)}{n(x)} \right) \right]
\]  (4.47)

This equation is known as the "Zeldowitch equation."

The boundary conditions are clearly indicated. There must be a cutoff on the size of droplet allowed in the system to keep the equilibrium distribution defined (required to preserve a constant total number of particles). This is carried into the rate theory demanding that
\[
f(G,t) = 0 \quad \text{for} \quad G > x^* > 1
\]  (4.48)

One also demands that
\[
f(i) = n(i)
\]  (4.49)

since the single molecules are virtually unaffected by the incipient nucleation process. These conditions imply that the molecules of each droplet of size $G$ removed are put back in as single molecules to conserve the total number of particles in the system and hence allow the use of the equation of continuity in the simple form above.

The equations derived include in their formalism the expression $n(x)$, an equilibrium expression. Once the nucleation process really begins, however, there are severe non-equilibrium conditions and one could not expect the equations to remain valid under these circumstances. One usually regards the equation as holding infinitesimally close to the point where the supersaturated state collapses. The closeness is determined by the degree of meaning which can be attached to $n(x)$ (a function of temperature and pressure), at any point
in the nucleation process.

The Zeldowitch equation is generally solved under the steady-state approximation:*  
\[
\frac{\partial f(x,t)}{\partial t} = 0 = \frac{\partial}{\partial x} \left[ \eta(x) \frac{\partial}{\partial x} \left( \frac{f(x,t)}{n(x)} \right) \right] 
\]  
(4.50)

This implies \( I = \text{constant} \) (from the equation of continuity Equation (4.46)).

Hence

\[
I = - n(x) s(x) \beta \frac{d}{dx} \left[ \frac{f(x)}{n(x)} \right] 
\]  
(4.51)

and by integration of (4.51):

\[
\left. \frac{f(x)}{n(x)} \right|_1^G = - \int_1^G \frac{I \, dx}{\beta n(x) s(x)} = - I \int_1^G \frac{dx}{\beta n(x) s(x)} 
\]  
(4.52)

\[
\frac{f(G)}{n(G)} - \frac{f(1)}{n(1)} = - I \int_1^G \frac{dx}{\beta n(x) s(x)} 
\]  
(4.53)

Using (4.48), (4.53) reduces to

\[
I = \frac{1}{\beta} \int_1^G \frac{dx}{n(x) s(x)} 
\]  
(4.54)

Since \( 1/n(x) \) goes through a very sharp and steep maximum at \( x = x^* \) one can expand \( 1/n(x) \) about \( x^* \) to obtain a Gaussian approximation.

Since the only region in which the integrand contributes to the integral is around \( x^* \), it is possible to write

\[
s(x) \approx s(x^*) 
\]  
(4.55)

and (4.54) becomes

\[
I \approx \frac{1}{\beta \cdot s(x^*)} \int_1^\infty \frac{dx}{n(x)} 
\]  
(4.56)

* A true steady state is required only when one desires to calculate \( f(x) \). The calculation of \( I^* \) can be made under a quasi-steady state approximation. See Chapter VI, section 5.
Let \( n(x) = n_1 \exp -\frac{1}{kT} \left[ \Delta \Phi(x) \right] \)

\begin{equation}
\approx n_1 \exp -\frac{1}{kT} \left[ \Delta \Phi(x^*) - \frac{1}{2} \Delta \Phi''(x^*) (x-x^*)^2 \right]
\end{equation}

Combining (4.56), (4.58), and integrating,

\begin{equation}
I^* = \frac{B \sqrt{\gamma}(x^*) n(x^*)}{\sqrt{\pi}} \gamma x^* \text{ where } \gamma x^* = \left[ \frac{1}{2} \Delta \Phi''(x^*) \right]^{\frac{1}{2}}
\end{equation}

This result is essentially that obtained by Becker and Döring (to within an order of magnitude which, as will be seen, is not a significant error).

If one expresses the rate, \( I^* \), in terms of the supersaturation ratio, \( (p/p\infty) \), and plots \( \ln I^* \) vs \( \ln (p/p\infty) \), a curve similar to Figure 31 is obtained. The extremely sharp variation in rate with \( \ln (p/p\infty) \) means that the phenomenon should appear to be critical in nature, the rate going from nearly zero to virtually \( \infty \) with a minute increment of pressure. Experimentally, this is observed for condensation phenomena. This sharpness, too, is an a posteriori justification of the use of a quasi-equilibrium equation almost up to the point of appreciable nucleation.

The nucleus size, \( x^* \), determines the rate, all other embryos being unimportant. One does not need to worry, then, about the use of \( \Omega \) for an embryo. The only droplet of importance is the nucleus which is an equilibrium droplet.

The predicted critical supersaturation ratios for various substances are shown in Tables 3 and 4 assuming the "critical" rate, \( I^* \), corresponding to the observed nucleation, is unity. The agreement with the experimental data of Volmer and Flood
FIGURE 31
is phenomenal!

5. Criticism of the Theory

In view of the seemingly striking success of the theory it is strange that even before new experimental evidence was found, severe criticism of the conceptual basis of the formulation arose as a result of the controversy between Pound and LaMer, and Kirkwood and Buff.

Before proceeding to enumerate these inherent difficulties (and those pointed out by other authors) it is profitable to examine the fundamental assumption of the thermodynamic analysis of Frenkel in the light of the rigorous Gibbs theory.

Frenkel asserts that the quantity

\[ \Phi = \Omega_1 \mu_1 (R, T) + \Omega_2 \mu_2 (P, T) + \sigma A \] (4.16)

is a thermodynamic potential for the system vapor plus droplet and further asserts that this is a Gibbs free energy of the system so that the equilibrium condition is given by Equation (4.17) This represents an approximation. The Gibbs theory for such a system yields the fundamental equation

\[ dU_T = TdS_T - P_1 dV_1 - P_2 dV_2 + \mu_1 dN_1 + \mu_2 dN_2 + \mu_s dN_s + \sigma dA \] (4.60)

where the dividing surface has been chosen to be the "Surface of Tension". In this case, application of Euler's Theorem to (4.60) yields

\[ U_T = TS_T - P_1 V_1 - P_2 V_2 + \mu_1 (T, P_1) N_1 + \mu_2 (T, P_2) N_2 + \mu_s (T, \sigma) N_s + \sigma A \] (4.61)

Let the quantity \( \Phi' \) be defined by

\[ \Phi' = U_T - TS_T - P_1 V_1 - P_2 V_2 - \mu_s (T, \sigma) N_s \]

\[ = \sigma A + N_1 \mu_1 (P_1, T) + N_2 \mu_2 (T, P_2) \] (4.62)
The Frenkel treatment requires that $\mu_2$ be a function of $p_1$. Hence,

$$
\mu_2(T, p_2) = \mu_2(T, p_1) + \int_{p_1}^{p_2} \vec{V}_2 dp
$$

(4.63)

which for an incompressible drop yields

$$
\mu_2(T, p_2) = \mu_2(T, p_1) + (p_2 - p_1) \vec{V}_2
$$

(4.64)

Therefore, combining (4.62) and (4.64), one obtains $\Phi$:

$$
\Phi = N_1 \mu_1(T, p_1) + N_2 \mu_2(T, p_1) + \nabla A = U_T - TS_T + p_1 \mu_1 + p_2 \vec{V}_2
$$

(4.65)

But $\vec{V}_2 N_2 = \vec{V}_2$ by definition and therefore (4.65) becomes

$$
\Phi = U_T - TS_T + p_1 \mu_1 + p_2 \vec{V}_2 - N_1 \mu_1(T, p_1) + N_2 \mu_2(T, p_1) + \nabla A
$$

(4.66)

Equation (4.60), yields

$$
d\Phi = -S_T dT + (p_1 - p_2) dV_2 + (V_1 + V_2) dp_1 - N_1 d\mu_1 + N_2 d\mu_2 + N_1 dN_1 + N_2 dN_2
$$

(4.67)

At equilibrium

$$
\mu_1(T, p_1) = \mu_2(T, p_2) = \mu s(T, \sigma) = \mu
$$

(4.3)

Hence

$$
d\Phi = -S_T dT + (p_1 - p_2) dV_2 + V_1 dp_1 - N_1 d\mu_1 + \mu (dN_1 + dN_2) + \nabla A
$$

(4.68)

For the Surface of Tension, a condition of equilibrium is

$$(p_2 - p_1) dV_2 = \nabla A
$$

(4.6)

Hence

$$
d\Phi = -S_T dT + V_1 dp_1 + \mu (dN_1 + dN_2) - N_1 d\mu_1
$$

(4.69)

In order that $(\Phi \Phi)_{T, p_1, N_T}$ be zero, as required by the Frenkel formulation, the condition

$$
N_1 \equiv 0
$$

(4.70)

must be satisfied. In this case

$$
dN_T = dN_1 + dN_2
$$

(4.71)
and

$$d\Phi = -S_\tau dT + V_\tau dP_1 + \mu dN_T$$  \hspace{1cm} (4.72)$$

The choice of \(N_s \equiv 0\), however, is equivalent to the choice of a new dividing surface and in particular, the \(r^* = 0\) surface. Thus, if one can ignore the distinction between the Surface of Tension and the \(r^* = 0\) surface (so that both \(\Theta_1 - \Theta_2 = 0\), \(\Theta_1 + \Theta_2 = 0\) and \(N_s \equiv 0\) are satisfied for a curved interface) then \(\Phi\) is indeed a thermodynamic potential for the system with the independent variable \(T\), \(P_1\), and \(N_T\).* Note that \(\Phi\) is not a Gibbs function since it cannot be expressed in the form

$$G = U + PV - TS$$

Another possible choice to effect approximately this result is to demand that for the Surface of Tension, \(\sigma\) be a constant. In this case, at constant temperature, \(d\mu_s = 0\); \(N_T\), however, is not \(N_1 + N_2\).

Thus

$$d\Phi = -S_\tau dT + \mu (dN_T - dN_s) + V_\tau dP_1$$  \hspace{1cm} (4.73)$$

and if \(dN_s \ll dN_2\)

$$d\Phi \approx S_\tau dT + \mu dN_T + V_\tau dP_1$$  \hspace{1cm} (4.72)**

The fundamental criticisms of the theory, chiefly due to Volmer (76h), Kirkwood and Buff (42b), Buff (11), and Reiss (66e) are the following:

* Buff has indicated that in the Becker-Döring theory this lack of distinction occurs though he does not exhibit any analysis (42a).
** Reiss (66g) has pointed out that in the approximate Frenkel formalism the constancy of \(\sigma\) must be asserted else \(\Phi\) is not a thermodynamic potential.
1. Since typical nuclei are so very small (<100 molecules) the applicability of macroscopic thermodynamic concepts is questionable. The essence of the thermodynamic treatment is the insignificance of the relative fluctuation \( \frac{1}{\sqrt{N}} \). This quantity varies as \( \frac{1}{\sqrt{N}} \) (where \( N \) is the number of molecules in the system) and when the system is a droplet with \( N \sim 100 \), the fluctuations are quite severe. Volmer has attempted to rationalize the thermodynamic analysis but can only present a plausibility argument.

2. The distinction between droplet and vapor molecules and consequently the definition of \( r \), the radius of the droplet, is very uncertain due to the relatively large thickness of the non-homogeneous transition layer compared with the radius of the droplet. The arbitrary location of the dividing surface in this layer may profoundly alter \( r \).

3. The Kelvin law in its usual form relates only to the Surface of Tension and the bulk value of \( \sigma \) can be applied only to this surface, the location of which cannot be obtained thermodynamically. The assumption that it is the radius gotten by assuming that each molecule has its bulk liquid molecular volume is questionable.

The last two criticisms are superfluous when applied to the crude Frenkel formalism since these distinctions are inherently ignored in the thermodynamic analysis. They become
meaningful only when a more rigorous thermodynamic formalism is employed.

4. The dependence of surface tension upon curvature is ignored though Tolman (73a) and Kirkwood and Buff (42a) have shown that \( \sigma \) should decrease with decreasing radius and should be significant if applied to droplets of the size under consideration. Buff has indicated how the Frenkel treatment can be extended to cover this situation and how the more rigorous treatment of Gibbs can be made to include this dependence (11). Reiss has shown that the approximate Frenkel potential is a potential only when \( \sigma \) is constant. Attempts such as those of Pound and LaMer to modify the crude Frenkel theory by inclusion of the curvature dependence are incorrect.

5. Various attempts have been made to modify the Kelvin law on the basis of a statistical analysis. Thus Kührt includes terms involving translational and rotational degrees of freedom for the embryo in the Kelvin law (44a) and derives a modified nucleation theory (44b). The results are not significantly different. Herzfeld and Reed (36) have attempted a similar treatment. These analyses do not account for the observed discrepancies.

6. Frenkel (22b) has noted that possibly other than spherical embryos are formed but he regards this as not a significant error. (The sphere has a minimum
area and, crudely, a minimum free energy and hence is the most stable configuration).

7. The use of a steady-state approximation in the Zeldowitch equation has been questioned (62a,38).

8. The influence of heating of the droplet due to condensation has been considered and will be discussed more fully in Chapter 5 as will criticisms of the steady-state approximation, both of which were formulated as a result of nucleation experiments carried out in wind tunnels (62a,38).

9. There is some question as to the correct value of $\gamma$, the condensation coefficient for the growth of embryos. One assumes it is unity but experimental values for bulk systems indicate a value closer to 0.01 (76c). Volmer has found an "error" in the Becker-Doring analysis which just compensates the omission of $\gamma \leq 10^{-5}$ (76p).

10. The criterion of condensation $I^* = 1$/cc/second has been questioned (34) though there appears to be no experimental evidence which uniquely supports this view.

11. The use of $B = \frac{P}{\sqrt{2\pi m k T}}$ for embryos may be questioned as it is derived for a planar macro surface and is independent of the embryo size.
V. NON STEADY STATE NUCLEATION

1. Introduction

The solution of the Zeldowitch equation (4.47) in the classical rate theory, is usually carried out under the approximation of a steady-state in which

\[ \frac{\partial f(x,t)}{\partial t} \equiv 0 \quad (4.50) \]

The nucleation rate, \( I \), is then a constant, independent of time and size. (See Chapter VI, section 5).

As noted earlier*, the application of the classical theory to describe the conditions under which water vapor condensation shocks would occur when expansions in wind tunnels were carried out was originally quite satisfactory but in later work on \( H_2O \) and in the extension to the condensation of the components of air itself (in supersonic wind tunnels), no such agreement with experiment was found. Condensation always occurred much later than predicted, if at all! The calculations did not take account of the possibility of foreign nucleation though little effort was expended to clean up the air used in the early experiments. Lees and Bogdonoff (47), in fact, introduced up to 2\% \( CO_2 \) with no noticeable effect. Later work indicates (62a), however, that this is probably the most important factor in determining the possibility of condensation shocks. The discrepancy then is even more severe than it would appear at first sight, since

* Chapter II, section 5.
foreign nuclei tend to promote rather than inhibit condensation. Several suggestions as to the cause of this discrepancy were put forth and in order to assess them adequately, it must be clear as to what the experiment actually determines (47). The essential procedure is to set up a very high velocity linear flow of matter in a tunnel by expansion of the gas through a nozzle. After the initial shock front has passed through the tube, a steady-state distribution of temperature and pressure is set up.* Due to the very high degree of expansion the temperatures reached are quite low, usually extending far below the boiling points of the gases. As a result, the possibility of supersaturation and condensation arises. The experiment differs from that in a cloud chamber in this important respect: in the steady-state, both nucleation and growth are occurring simultaneously at every point in the tube. As a consequence, the first nuclei formed which grow, remove vapor from the adjacent mass moving down the tube but nucleation is still occurring. One therefore computes the mass of gas removed by nucleation and growth as a function of the distance from some fixed point (where there has been no mass diminution from the vapor, for example, at the nozzle). At some point, the mass condensed reaches a sufficient value to cause a shock. The theoretical criterion for such a shock is that the heat of condensation be some fraction of the

* Matter in a given volume element passes through the tube in about $10^{-5}$ seconds.
stagnation enthalpy (70). The analysis is clearly dependent upon the calculation of the rate of growth of nuclei.

The failure of the theory may then be due to several causes:

a. The inadequacy of the growth calculation for particles of nuclear dimensions.

b. The failure of the theoretical criterion for condensation shock.

c. The failure of the Volmer theory to describe the nucleation process.

The most popular criticism of the theory has been (c) - the breakdown of the Volmer theory. The difficulty was thought to arise in the steady-state approximation*. In the following sections the various proposed solutions will be examined and an approximation method will be introduced and used to solve the equation.

2. The Early Approximations

The first general non steady-state solution was proposed by Zeldowitch (84a) who, on the basis of simplifying assumptions, derived the relation

$$I_4 = I \exp \left( -\frac{x^*}{\theta s(x^*)} t \right)$$  \hspace{1cm} (5.1)

where $I = \text{steady state rate given by Equation (4.59)}$.

* Bogdonoff and Lees, however, felt that the basic thermodynamic structure broke down at some point (the continuum concept of the fluid state was no longer valid) and tried to reformulate the problem in terms of a cutoff size below which the Kelvin law had to be abandoned. The procedure is quite arbitrary.
Turnbull (74) has carried out numerical investigations for solid-solid transitions using some appropriate value for $\beta$.

The first attempt to calculate the transient specifically for the vapor nucleation problem was due to Kantrowitz (38). He suggested that there might be a time lag in the approach to the steady state distribution of embryos of particular importance in wind tunnel experiments due to the very short times involved. He further suggested that the heating of the embryos by molecular bombardment (heat of condensation) must be taken into account. Thus, if one writes the Zeldowitch equation, Equation (4.47), using for $n(x)$, (4.57), it becomes

$$\frac{\partial f(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ D(x) \frac{f(x,t)}{n(x)} \right] + \frac{1}{\nu_T} \frac{\partial}{\partial x} \left[ D(x) f(x,t) \frac{df(x,t)}{dx} \right]$$

where

$$D(x) = \beta S(x)$$

(5.3)

The approximations introduced by Kantrowitz consist in omitting the 2nd term on the right hand side of (5.2) and modifying the value of the evaporation coefficient $\alpha_x$ from

$$\alpha_x = \beta \exp \left[ \frac{-\Delta \phi}{\nu_T} \right]$$

(which is $\beta$ for $x = x^*$, the nucleus) to

$$\alpha'_x = \alpha_x \left[ 1 + \Theta \left( \frac{U_0}{R_T^2} - \frac{1}{2T} \right) \right]$$

(5.4)

where $\Theta =$ Temperature difference between droplet and ambient temperature.

$U_0 =$ Latent heat of vaporization of the liquid droplet.

Probstein (62b) in a more refined analysis kept part of the term omitted by Kantrowitz but also included the corrected value of $\alpha'_x$.

These analyses, therefore, are devoid of meaning, not
simply because of the omission of terms in the equation, but
due to the introduction of a corrected value of $\alpha_x$. The
theory is an equilibrium theory; the quantity $n(x)$ appears.
It is fundamental for a system in thermodynamic equilibrium
(in which the $n(x)$ is definable) that the temperature in the
system be uniform. Any attempt to introduce temperature
corrections into an equilibrium theory cannot be correct (31).

Collins (14) formulated a solution of the time dependent
Zeldowitch equation but assumed that the region of importance
in the solution was that about the nucleus and hence set
$D(x) = D(x^*)$.

He found for the rate of passage of embryos through
the nucleus size $I^*(t)$,

$$I^*(t) = -D^* \left[ \frac{\partial \Phi}{\partial Y} \right]_{x=x^*} \left( x^* \right)$$

$$= N_0 \exp \left[ \frac{4\Phi(x^*)}{kT} \right] \exp \left[ \frac{2\pi i}{2\hbar} \right] \left[ \frac{D^*}{\pi i} \right]$$

which for short times may be written

$$I^*(t) \approx \left[ \frac{2 N_0 \exp \left[ \frac{4\Phi(x^*)}{kT} \right] \exp \left[ \frac{2\pi i}{2\hbar} \right] \left[ \frac{D^*}{\pi i} \right] \left[ \frac{D^*}{\pi i} \right] \right]$$

where

$$Y(x) = \int_{x^*}^{x} \frac{\exp \left[ \frac{4\Phi(x)}{kT} \right] \exp \left[ \frac{2\pi i}{2\hbar} \right] \left[ \frac{D^*}{\pi i} \right] \left[ \frac{D^*}{\pi i} \right]}{D(x)} \, dx$$

$$t = -\left[ \frac{1}{\left( \frac{d^2\Phi}{dx^2} \right)} \right]_{x=x^*} = \frac{2}{3} \pi A \left( \frac{2M}{4\pi \rho} \right) \sigma \left( x^* - \frac{4}{3} \right)$$

It was desirable to test the error introduced by the use
of $D(x) = D(x^*)$ and, at the same time, obtain expressions for
$f(x,t)$ and the flux in the region before any appreciable
number of nuclei are formed. Since $D(x)$ is not constant, an
approximation scheme had to be employed. In the following
section the method will be described in some detail for a simple case. Following that, the nucleation problem will be formulated and solved.

3. The Approximation Scheme of Reiss

The method is a generalization of one previously employed by Reiss (66b) but apparently first due, in very crude form, to Rashevsky (64). Landahl (46) has recently presented a systematic survey of an extension of the Rashevsky method but it is not nearly as general as the current formulation developed by Reiss (66c) since one must assume the precise functional form of the answer and certain average properties of the system must be known (or defined).

The basis of the method rests upon an analysis of the physical situation rather than upon any well-defined sequence of mathematical steps; by a plausibility argument it can be shown how the method is related to exact formulation.

Consider the case of ordinary diffusion from an infinite reservoir, at \( x = 0 \), into a semi-infinite region (with no sources or sinks). The problem may be defined formally by the set of equations

\[
\begin{align*}
D \frac{\partial^2 c(x,t)}{\partial x^2} &= \frac{\partial c(x,t)}{\partial t} \\
C(x,0) &= C_0 \\
C(\infty, t) &= 0 \\
\end{align*}
\]

(5.10)

The exact solution is easily generated by the method of integrals (12a) and is found to be (12b)

\[
C(x,t) = C_0 \left[ 1 - \int_0^x e^{-\frac{x^2}{4Dt}} \, dx \right] = C_0 \text{erfc} \left[ \frac{x}{2\sqrt{Dt}} \right]
\]

(5.11)
The series expansion, to the first term, is
\[ C(x,t) = C_0 \left(1 - \frac{x}{\sqrt{\pi D t}} \right) = C_0 \left(1 - \frac{x}{1.73 \sqrt{D t}} \right) \quad (5.12) \]
and is valid when \( x/(\sqrt{D t})^k \) is small compared to unity.

Consider the actual physical situation. Material is diffusing into the region from an infinite reservoir, the concentration at the boundary being fixed at \( C_0 \). The total amount of material passing into the region from time \( t = 0 \) to \( t = t \) is given by the integral, over time, of the flux at the boundary, \( I_0 \), multiplied by the boundary cross-sectional area, \( A \).

Thus
\[ \text{Total mass input} = \int_0^t I_0 A \, dt = \int_0^t DA \left( \frac{\partial C}{\partial x} \right)_{x=0} \, dt \quad (5.13) \]
The mass in any volume element, \( Adx \), in the region is given by \( C(x,t)Adx \). The total mass in the region is then given by the integral
\[ \int_0^\infty A \, C(x,t) \, dx \quad (5.14) \]
(where the \( \infty \) limit arises due to the use of a semi-infinite region as the diffusion field). Hence, from the law of conservation of matter (with no sinks or sources in the region)
\[ \int_0^t D \left( \frac{\partial C}{\partial x} \right)_{x=0} \, dt = \int_0^\infty C(x,t) \, dx \quad (5.15) \]
Suppose one were to define the quantity \( \eta(t) \) by the relation
\[ \int_0^t D \left( \frac{\partial C}{\partial x} \right) \, dt = \int_0^{\eta(t)} C(x,t) \, dx \quad (5.16) \]
where \( \left( \frac{\partial C}{\partial x} \right) \) is not evaluated at the boundary but at any point \( x \). In order to preserve the conservation of mass, no material can be located beyond \( \eta(t) \). Hence
\[(x, t) = 0 \quad x \gg \eta(t) \quad (5.17)\]

Obviously, from the definition, (5.16),

\[\eta(0) = 0 \quad (5.18)\]

This approximation, based on an analogy with the exact physical analysis, implies directly the form of \(C(x, t)\). Thus

\[\int_0^{\eta(t)} C(x, t) \, dx = Q(t) = \text{a function of time} \quad (5.19)\]

and therefore

\[\int_0^{\tau} \partial \left( \frac{\partial C}{\partial x} \right) \, dt = Q(t) \quad (5.20)\]

Hence \(\partial C / \partial x\) is a function of time and

\[C(x, t) = A(t) + x \cdot B(t) \quad (5.21)\]

Note that this approximation essentially asserts that the flux is uniform spatially over the region but not in time.

The original formulation of Reiss used the condition,

\[\left( \frac{\partial C}{\partial t} \right) = 0 \quad (5.22)\]

and derived from

\[D \left( \frac{\partial^2 C}{\partial x^2} \right) = 0 \quad (5.23)\]

the relation

\[C(x, t) = A(t) + x \cdot B(t) \quad (5.21)\]

The conservation condition together with the condition \(c(\eta, t) = 0\), was then invoked to define the problem, since the conditions

\[C(x, 0) = 0 \quad x > 0 \quad ; \quad C(\infty, t) = 0 \]

cannot be met by a linear approximation. \(C(o, t) = C_0\) can, of course, be satisfied.

The specific form of \(C(x, t)\) may easily be generated:

\[C(x, t) = A(t) + x \cdot B(t) \quad (5.21)\]
From (5.10)

\[ C_0 = C(0, t) = \Phi(t) \]  
\[ \text{(5.24)} \]

From (5.17) \( C(t, t) = 0 = C_0 + B(t) \eta(t) \).

Therefore

\[ B(t) = - \frac{C_0}{\eta(t)} \]  
\[ \text{(5.25)} \]

and

\[ C(x, t) = C_0 \left[ 1 - \frac{x}{\eta(t)} \right] \]  
\[ \text{(5.26)*} \]

Now from (5.15) and (5.26)

\[ - \int_0^t B \left[ - \frac{C_0}{\eta(t)} \right] dt = C_0 \int_1^\eta \left[ 1 - \frac{x}{\eta(t)} \right] dx \]  
\[ \text{(5.27)} \]

Therefore

\[ \int_0^t B \frac{C_0}{\eta(t)} dt = \frac{C_0 \eta(t)}{2} \]  
\[ \text{(5.28)**} \]

Differentiate (5.28) with respect to time:

\[ \frac{d}{dt} \frac{C_0}{\eta(t)} = \frac{C_0}{2} \frac{d \eta(t)}{dt} \]  
\[ \text{(5.29)} \]

Solution of the ordinary differential equation (5.29) subject to (5.18) yields

\[ \eta = \pm 2 \sqrt{<t} \]  
\[ \text{(5.30)} \]

Hence

\[ C(x, t) = C_0 \left[ 1 - \frac{x}{2 \sqrt{<t}} \right] \]  
\[ \text{(5.31)} \]

(since the positive root of \( \eta \) would imply that the concentration in the region was increasing over that at the boundary.)

The schematic form of the solution is shown in Figure 32.

The approximation to the exact solution yielded Equation (5.12) which is very close to the approximate result.

* This is the precise form which Landahl assumes.

** This relation is also assumed by Landahl.
There has been no rigorous validation of the technique, though in every case for which the exact solution is known, to which the method has been applied, the first approximation to the exact solution is obtained (66c).

It was felt, therefore, that a good approximation to the exact solution of the Zeldowitch equation could be obtained, and hence \( f(x,t) \) and \( I(t) \) evaluated, without assuming \( D(x) = D(x^*) \).

4. The Non-Steady-State Zeldowitch Equation

The exact problem is defined by

\[
\frac{\partial f}{\partial t} = \frac{\partial}{\partial x} \left[ D(x) N(x) \frac{\partial}{\partial x} \left( \frac{f(x,t)}{N(x)} \right) \right] \tag{4.47}
\]

\[ f(x, t) = 0 \quad \text{if } G > x^* \tag{4.48} \]

\[ f(1, t) = N(1) = \text{constant} \tag{4.49} \]

where

\[ N(x) = N_0 \exp \left( ax + bx^{2/3} \right) \tag{5.32} \]

\[ D(x) = \eta x^{2/3} \tag{5.33} \]

The approximate solution may be expressed as the solution of the following equations:

\[
\int_0^t \mathcal{I}(t) \, dt = \int_1^{X(t)} f(x,t) \, dx \tag{5.34}
\]

\[ f(X, t) = 0 \tag{5.35} \]

\[ f(0) = 1 \tag{5.36} \]

\[ f(1, t) = N(1) \tag{4.49} \]

where the approximation that \( I = I(t) \) only has been explicitly included. (5.34) implies that

\[
\mathcal{I} = \mathcal{I}(t) = -N(x) D(x) \frac{\partial}{\partial x} \left[ \frac{f(x,t)}{N(x)} \right] \tag{5.37}
\]
and hence
\[ \frac{\partial}{\partial x} \left( \frac{f(x,t)}{N(x)} \right) = - \frac{I(t)}{N(x) D(x)} \] (5.38)

Integrate (5.38) with respect to \( x \):
\[ \int_1^x \frac{\partial}{\partial x} \left[ \frac{f(x,t)}{N(x)} \right] dx = \int_1^x \frac{-I(t)}{N(x) D(x)} dx + B(t) \] (5.39)

where \( B(t) \) is some arbitrary function of time.

Then, using (4.49)
\[ \frac{f(x,t)}{N(x)} - 1 = \int_1^x \frac{I(t)}{N(x) D(x)} dx + B(t) \] (5.40)

and to satisfy (4.49)
\[ B(t) = 0 \] (5.41)

Hence
\[ f(x,t) = N(x) \left[ 1 - \int_1^x \frac{I(t)}{N(x) D(x)} dx \right] \] (5.42)

Let \( N(x) = N_1 \Phi(x) \) (5.43)

and \( F(x) = \int_1^x \frac{dx}{\Phi(x) x^{1/2}} \) (5.44)

Then, using (5.33), (5.42) becomes
\[ f(x,t) = N_1 \Phi(x) \left[ 1 - \frac{I(t) F(x)}{N_1 \eta} \right] \] (5.45)

From (5.34) and (5.45) we obtain
\[ \int_0^t I(t) dt = \int_1^x \frac{\Phi(x) F(x) dx}{\eta} - \int_1^x \frac{\Phi(x) F(x) I(t)}{\eta} dx \] (5.46)

Differentiate with respect to time:
\[ I(t) = \frac{N_1 \Phi(x) dx}{dt} - \int_1^x \frac{\Phi(x) F(x) dx}{\eta} \frac{dt}{dx} dx - \frac{\Phi(x) F(x) I(t)}{\eta} \frac{dx}{dt} \] (5.47)

But from (5.35)
\[ f(K,0) = 0 = N_1 \Phi(K) \left[ 1 - \frac{I(t) F(x)}{\eta} \right] \] (5.48)
hence
\[ I(t) = \frac{N_1}{F(K)} \]  

(5.49)

From Equation (5.49) \( \frac{dI}{dt} \) may be obtained:
\[ \frac{dI}{dt} = -\frac{N_1}{[F(K)]^2} \frac{dF}{dK} \frac{dK}{dt} \]  

(5.50)

Hence, from (5.47) and (5.50)
\[ I(t) = \frac{N_1}{[F(K)]^2} \left[ \frac{dF}{dK} \int_1^K \Phi(x) F(x) dx \right] \frac{dK}{dt} \]  

(5.51)

Equating (5.49) and (5.51), we obtain
\[ \frac{dK}{dt} = \frac{\eta}{\frac{d\ln F(K)}{dK} \int_1^K \Phi(x) F(x) dx} \]  

(5.52)

This ordinary differential equation is separable:
\[ \int_0^t \frac{d\tau}{\eta} = \frac{1}{\frac{d\ln F(K)}{dK} \int_1^K \Phi(x) F(x) dx} \int_1^K \Phi(x) F(x) dx d\tau \]  

(5.53)

Therefore,
\[ t = \frac{1}{\eta} \left[ \frac{d\ln F(K)}{dK} \int_1^K \Phi(x) F(x) dx \right] d\tau \]  

(5.54)

(5.54) may be integrated by parts:
\[ \text{if } U = \int_1^K \Phi(x) F(x) dx \]  

(5.55)

and
\[ dV = \frac{d\ln F(K)}{dK} d\tau \]  

(5.56)

then
\[ t = \frac{1}{\eta} \ln F(K) \left[ \int_1^K \Phi(x) F(x) dx \right] - \int_1^K \Phi(x) F(x) dx d\tau \]  

(5.57)

Unfortunately, the integrals do not admit of an analytic evaluation and must be evaluated numerically.

From the numerical solution of (5.57), one obtains \( K(t) \) and hence \( I(t) \) may be computed from (5.49).

To facilitate the calculation, it is advisable to change variable:
Let \( q = z^3 \), \( \kappa(t) = \mathcal{Z}_0(t)^3 \) \( (5.58) \)

whence \((5.57)\) becomes

\[
t = \frac{3 \ln F(\mathcal{Z}_0)}{\eta} \int_{\mathcal{Z}_0(t)}^{\mathcal{Z}_0(t)} z^2 h(z) \left[ 1 - \frac{\ln F(z)}{\ln F(\mathcal{Z}_0)} \right] dz \quad (5.59)
\]

where

\[
F(\mathcal{Z}_0) = h(\mathcal{Z}_0) \exp \left( -a \mathcal{Z}_0^3 - b \mathcal{Z}_0^2 \right) = 3 \int_{\mathcal{Z}_0}^{\mathcal{Z}_0} e^{-a \mathcal{Z}_0^3 - b \mathcal{Z}_0^2} d \mathcal{Z}_0 \quad (5.60)
\]

and

\[
a = \sqrt[3]{\frac{\ln p}{p^\infty}} \quad (5.61)
\]

\[
b = -\frac{4\pi \tau}{\kappa T} \left[ \frac{3M}{4\pi p} \right]^{2/3} \quad (5.62)
\]

and

\[
\eta = \frac{4\pi p}{(2\pi m \nu c)^2} \left( \frac{3M}{4\pi p} \right)^{2/3} \quad (5.63)
\]

The integrals \( F(Z) \) and \( F(\mathcal{Z}_0) \) may be evaluated conveniently in the following fashion \((32)\). Let

\[
F(z) = h(z) \exp \left( -a z^3 - b z^2 \right) \quad (5.64)
\]

Obviously \( h(1) = 0 \) (from \((5.60)\))

Differentiate \((5.64)\) with respect to \( Z \):

\[
dh/dZ = 3 - h \left( -3a z^2 - 2b z \right) \quad (5.65)
\]

Solution of this equation with \( h(1) = 0 \) will yield the desired integral.

The differential equation was solved numerically for two cases using the method outlined by Hartree \((32)\). The initial values were checked by the more exact Runge Kutta method \((49)\) and found to be in excellent agreement with the method of Hartree.

The final integrals for the time, \( t \), were evaluated at intervals of 0.1 in \( Z \) using Weddles Rule \((15)\).
5. Results

For $N_2$ at 76.81°C and $\ln p/p_\infty = 1$ and $\ln p/p_\infty = \frac{1}{2}F(Z)$ was obtained (Table 15). In this case

\[ \sigma = 8.97 \text{ dynes/cm}^2 \]  
\[ p_\infty = 715.1 \text{ mm} \]  
\[ \rho = 812 \text{ gms/cc} \]

For $\ln p/p_\infty = 1$ and for $\ln p/p_\infty = \frac{1}{2}$

\[ p = 1943.1 \text{ mm} \]  
\[ a = 1 \]  
\[ b = -6.084 \text{ molecules}^{1/3} \]  
\[ \eta = 1.058 \times 10^{10} \]  
\[ p = 1178.7 \text{ mm} \]  
\[ a = \frac{1}{2} \]  
\[ b = -6.084 \text{ molecules}^{1/3} \]  
\[ \eta = 6.417 \times 10^{9} \]

The results of the calculation of the flux, $I(t)$, are shown in Table 16 and illustrated in Figure 33. For comparison, the results obtained from the short-time approximation of Collins are also plotted (see Table 17).

At first sight, there is a very severe discrepancy between the two calculations but this is only illusory.

Thus, consider the expression for the flux:

\[ I(x,t) = -N(x)p(x) \frac{2}{N(x)} \left[ \frac{f(x,t)}{N(x)} \right] \]  
\[ = \frac{d(x)}{f(x,t)} \frac{d\ln N(x)}{dx} - D \frac{\partial f(x,t)}{\partial x} \]  
\[ (5.37) \]

Collins has calculated $I(x*,t)$ which is correctly defined as the nucleation rate: the rate of passage of embryos through the nuclear size. At $x = x*$

\[ \frac{d\ln N(x)}{dx} = 0 \]  
\[ (4.31) \]

and hence

\[ I(x*,t) = -D \left[ \frac{\partial f(x,t)}{\partial x} \right]_{x=x*} \]  
\[ (5.67) \]

We have calculated $I(x,t)$ and hence included the extra term

\[ -D(x) f(x,t) \frac{d\ln N(x)}{dx} \]
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TABLE 16

Approximate Time Dependence of Flux I(t)

<table>
<thead>
<tr>
<th>t(sec)</th>
<th>ln p/p∞ = 1</th>
<th>ln p/p∞ = 1/2</th>
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<tr>
<td>1.9x10^-10</td>
<td>2.5x10^29</td>
<td>2.3x10^-9</td>
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<tr>
<td>1.23x10^-9</td>
<td>1.8x10^26</td>
<td>1.7x10^-8</td>
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<tr>
<td>3.2 x &quot;</td>
<td>1.5x10^23</td>
<td>5.7x &quot;</td>
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<tr>
<td>7.7 x &quot;</td>
<td>5.4x10^20</td>
<td>1.4x10^-7</td>
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<tr>
<td>1.26x10^-8</td>
<td>2.2x10^19</td>
<td>2.5x &quot;</td>
</tr>
<tr>
<td>1.6 x &quot;</td>
<td>9.8x10^18</td>
<td>3.6x &quot;</td>
</tr>
</tbody>
</table>

TABLE 17

Short Time Approximation (Collins) to I*(t)

<table>
<thead>
<tr>
<th>t(sec)</th>
<th>ln p/p∞ = 1</th>
<th>ln p/p∞ = 1/2</th>
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<tbody>
<tr>
<td>10^-10</td>
<td>9.3x10^-12</td>
<td>1.6x10^-49</td>
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<tr>
<td>10^-9</td>
<td>2.3x10^-16</td>
<td>4.4x10^-27</td>
</tr>
<tr>
<td>10^-8</td>
<td>4.5x10^-18</td>
<td>2.7x10^-25</td>
</tr>
<tr>
<td>10^-7</td>
<td>2.7x &quot;</td>
<td>1.5x &quot;</td>
</tr>
<tr>
<td>10^-6</td>
<td>9.2x10^17</td>
<td>4.8x10^-26</td>
</tr>
</tbody>
</table>
To reconcile the two points of view, it must be recalled that in this approximation there are no nuclei until a time 
\[ t_x^* \] where
\[ |\chi(t_x^*)| = |x^*| \]
since \( f(K,t) = 0 \) \( x \gg K \).
Thus for all \( t < t_x^* \), \( I(x^*,t) \) in this approximation is zero. At \( t = t(x^*) \) the calculations of Collins and this calculation should agree and they do! (See Figure 34).

From the definition of the rate (in this approximation) (5.49) it is apparent that when |\( K \) reaches |\( x^* \) (that is \( t = t_x^* \)) the value of the integral \( F(K) \) cannot increase significantly since the integrand for \( |K| > |x^*| \) tends to vanish. Therefore, \( I(t) \) is constant for all \( t > t_x^* \). This is the steady state. The correct steady state solution is indeed given by the approximation since (5.49) reduces to (4.59) when \( |K| > |x^*| \).

The initially huge flux found in this calculation merely reflects the very great concentration gradient at the boundary \( x = 1 \), at time zero. As time goes on and the concentration of embryos in the region rises, the reverse reactions (decay of embryos) begin to take hold and the return flux becomes important. Eventually, a steady state is reached.

It is of interest to compute \( f(x,t) \) to observe the buildup to the steady state. \( f(x,t) \) is given by
\[
 f(x,t) = N(x) \left[ 1 - \frac{F(x)}{F(K)} \right] \quad (5.68)
\]
TIME DEPENDENT CRITICAL RATES

FIGURE 34
and the cases of interest are illustrated in Figure 35. Naturally, when \( |x| = |K| \), \( f(x,t) \) vanishes, since this was a boundary condition.

6. Conclusions

The results obtained indicate that the buildup to the steady state occurs several orders of magnitude more rapidly than the times involved in the wind tunnel experiments. It would thus appear that the cause of the discrepancy lies elsewhere, probably in the growth calculations which are very crude.

The method of analysis should prove useful in nucleation problems in which transients are important i.e. solid-solid transitions.
\[ \frac{f(x,t)}{N(0)} \]

\[ X = X^3 \]

FIGURE 35

\[ \ln \frac{V}{P_{\infty}} = 1 \]

\[ 1.9 \times 10^{-10} \text{ sec.} \]

\[ 3.2 \times 10^{-9} \text{ sec.} \]

\[ 1.6 \times 10^{-8} \text{ sec.} \]
VI. KINETICS OF NUCLEATION OF SYSTEMS UNDERGOING ASSOCIATION: MONOMER-DIMER EQUILIBRIUM

1. Introduction

A great part of the current controversy over the validity of the quantitative B.D.Z. theory stems from the fact that the theory is apparently confirmed quite exactly by the experimental measurements of Volmer and Flood (76n) though, in principle, there are severe conceptual difficulties in its formulation and application (as indicated in Chapter IV).

In the discussion of the experimental research (Chapter III), the possibility that the Volmer-Flood experiments represent heterogeneous nucleation on ions has been considered. The general concept of the need for very careful comparison of theory and experiment has been emphasized throughout. So far, the discrepancy has been attributed to the unsuspected presence of impurity but there is another, equally logical, possibility. The clue lies in the fact that for one substance, methyl alcohol, there is no agreement between theory and experiment. (The experimental error for ethyl acetate is sufficiently large to consider the results unreliable).

If one examines the substances investigated by Volmer and Flood, particularly water and several lower alcohols, it is seen that they are substances which associate in the vapor phase; this has been experimentally observed to the extent of measuring the equilibrium constant of the reaction (88). The vapors investigated in the nucleation experiments then, should contain some fraction of molecules in the form of
dimers or higher polymers.

The basic premise of the rate theory, however, asserts that embryos grow and decay by the addition and loss of single molecules: collisions between embryos are extremely rare. If the dimer concentration is appreciable, it should influence the rate of nucleation since the fluctuation process to form nuclei can now proceed in steps of two molecules; the initial step of forming embryos of size 2 being an already accomplished fact. It has been pointed out by Volmer (761) that the collision of two molecules to yield an embryo of size 2 is energetically unfavorable.

It is then quite possible that the theory and experiment do indeed diverge badly; not due to impurity, but due to an incorrect theoretical analysis involving neglect of the chemical reaction (association) in the vapor phase. One would expect, a priori, that the presence of dimers would favor the condensation of the supersaturated vapor causing a lower critical supersaturation ratio. The experimental results of Volmer and Flood for critical supersaturation ratios would then be higher than would be predicted by the correct application of the theory.

It was decided to carefully investigate nucleation in a system in which a monomer-dimer equilibrium could exist and determine whether or not the Volmer-Flood data did indeed agree with the prediction of the theory.

As this research was completed, an analysis of a closely
related problem was described by Frisch and Willis (24b). Comment on their work will be deferred until later except to note that their conclusions do not refer to a situation in which a true monomer-dimer equilibrium exists but rather to the perturbing effects of collisions between single molecules and embryos of size 2. These are not the same.

2. The Vector Method.

The problem may be regarded, formally, as a two component nucleation phenomenon, a general formulation and solution of which has been given by Reiss (66a). In the case of monomer-dimer equilibrium it is not necessary to utilize the complete analysis of Reiss but the concept of the vector flow is invaluable for the systematization of the detailed molecular mechanism. A similar method finds application in the study of the nucleation of crystal faces (76j).

Assume that the monomer and dimer molecules in the vapor phase can be regarded as separate entities and that, formally, each embryo may be regarded as specified when the net number of monomer and dimer additions (denoted by m and d, respectively) necessary to form the embryo are indicated. Each such embryo may be represented by a point on a lattice, the coordinates of each point being the net number of monomer and dimer steps necessary to form the embryo (Figure 36).*

The fundamental problem is the calculation of the rate

* There is no point (0,0) since no embryo is defined there.
of passage of embryos through the nucleus size. It is clear that one is not interested in embryos specified by \((m,d)\) but rather in embryos of a given size, \(x\), where \(x = m + 2d\). This arises from the fact that in the liquid embryo, distinction between monomer and dimer would be physically meaningless. (It is not meaningless in the vapor!) The quantity of interest is then the number of embryos which pass through the size \(x^*\), the nucleus size, by impact of either a monomer or a dimer.

It is possible to regard the flow through a given size \(x\) as composed of two flows, one due to monomer impact and the other due to dimer impact on the embryos. These flows can be represented by vectors on the embryo plane of Figure 36 and a total flow vector defined in terms of these.

Let \(J_m(d)\) be the flow through the size \((m,d)\) due to monomer impact on embryos of size \((m,d)\) and \(J_d(m)\) the flow through the same embryo size due to dimer impact. The total flow in which we are interested is the flow through the size \(x^*\). This is represented on the embryo plane by the total flow over the line

\[
x^* = (m + 2d)_x
\]

(6.1)

All impacts which lead to a crossing of the line \(x^*\) contribute to the nucleation rate.

The problem is completely defined when the conditions on the boundaries of the \((m,d)\) plane are specified.

3. Boundary Conditions

The boundary conditions of the problem are formulated from
the physical situation. By analogy with the one component case one cannot allow embryos of size larger than some value $G$ where $G > x^*$, the nucleus size.

Thus

$$f(G, d, t) = 0$$

(6.2)

$$f(m, G, t) = 0$$

(6.3)

In the vector scheme, one cannot allow net flow across the boundaries. Hence

$$J_m (m, d, t) \big|_{m=0} = 0$$

(6.4)

$$J_d (m, d, t) \big|_{d=0} = 0$$

(6.5)

Finally, the concentrations of monomer and dimer are fixed at their equilibrium value and the conditions

$$f(l, l, t) / n(l) = 1$$

(6.6)

$$f(m, l, t) / n(l) = 1$$

(6.7)

are imposed.

4. Formulation

Let $n(m, d)$ represent the equilibrium number of embryos composed of $m$ monomer and $d$ dimers*, in equilibrium with a gas phase in which monomers and dimers, at partial pressures $P_m$ and $P_d$, exist at the temperature $T$. (Any effect on $P_{\text{total}}$ due to changes in embryo concentration, which may alter $P_m$ and $P_d$, are neglected). In the liquid embryo monomer and dimer are indistinguishable and hence the quantity of interest,

---

* Equivalent to "having been formed of m monomer and d dimer steps".
n(x), is defined by

$$\sum_{m+2d=x} a(m,d) = n(x)$$  \hspace{1cm} (6.8)

where \( x = m + 2d \), the number of molecules in the embryo.

Let \( J_d(m) \) equal the flux through dimers at a given monomer concentration in the embryo. By analogy with the equation (4.40)

$$J_d(m) = \beta_d s(m,d) f(m,d,t) - \alpha_d(m,d+1,t) s(m,d+1) f(m,d+1,t)$$  \hspace{1cm} (6.9)

where \( f(m,d,t) \) is the non-equilibrium distribution of embryos of size \((m,d)\) at time \( t \) and \( s(m,d) \) is the surface area of the embryo of size \((m,d)\). This latter can only depend upon the total number of molecules in the embryo (when incompressible) and hence must be of the form

$$s(m,d) = s(x) = s(m + 2d)$$  \hspace{1cm} (6.10)

At equilibrium, by the principle of detailed balance,

$$J_d(m) = 0$$  \hspace{1cm} (6.11)

Therefore from (6.9)

$$\alpha_d(m,d+1) s(m+2(d+1)) n(m,d+1) = \beta_d s(m+2d) n(m,d)$$

Summing over \( x \)

$$\sum_{m+2d=x} \alpha_d(m,d+1) s(x+2) n(m,d) = \sum_{m+2d=x} \beta_d s(x) n(m,d)$$

Since \( \sum_{m+2d=x+2} = \sum_{m+2d=x} \)

If \( \alpha_d(m,d+1) \) is assumed to be constant for a given \( x \) (that is, \( \alpha_d(m,d+1) = \alpha_d(x+2) \)) which is consistent with the concept of indistinguishability in the liquid phase, then

$$\alpha_d(x+2) = \frac{\beta_d s(x) n(x)}{s(x+2) n(x+2)}$$  \hspace{1cm} (6.12)
Then

$$J_d(m,d,t) = \beta_d \delta(x) n(x) \left[ \frac{f(m_d,t)}{n(x)} - \frac{f(m_d+1,t)}{n(x+2)} \right]$$ (6.13)

$$= -\beta_d n(x) \delta(x) \left[ \frac{f(m_d,t)}{n(x)} \right]_m$$ (6.14)

A similar expression for $J_m(d)$ may be derived.

$$J_m(m_m,d,t) = -\beta_m \delta(x) n(x) \left[ \frac{f(m_d,t)}{n(x)} \right]_m$$ (6.15)

The expressions for $J_m(d)$ and $J_d(m)$ can be integrated: at constant $m$ (6.14) yields

$$\frac{f(m_d,t)}{n(m+2d)} \bigg|_0^G = -\int_0^G \frac{J_d(m_d,t)}{n(x) \delta(x) \beta_d} \, dd \quad G > x^*$$ (6.16)

Therefore

$$\frac{f(m_G,t)}{n(G)} - \frac{f(m_0,t)}{n(0)} = -\int_0^G \frac{J_d(m_d,t)}{n(x) \delta(x) \beta_d} \, dd$$ (6.17)

From (6.3) $\frac{f(m,G,t)}{n(G)} = 0$. Therefore (6.17) reduces to

$$\frac{f(m_0,t)}{n(0)} = \int_0^G \frac{J_d(m_d,t)}{n(x) \delta(x) \beta_d} \, dd$$ (6.18)

Since at $x^*$, $1/n(x)$ has a very steep maximum, one can expand $n(x)$ about $x^*$ and perform a peak integration. (Only in the region of $x^*$ is the integral significantly different from zero). It is further assumed that

$$\delta(x) \approx \delta(x^*)$$ (6.19)

$$J_d(m_d,t) \approx J_d\left(m, \frac{x^*-m}{2}, t\right) = J_d^*(m)$$ (6.20)

Therefore

$$\frac{f(m_0,t)}{n(0)} = \frac{J_d^*(m)}{\beta_d \delta(x^*)} \int_0^G \frac{dd}{n(x)}$$ (6.21)
At constant $m$, the variable of integration may be changed:

$$x = m + 2d$$

when $d \to 0$, $x \to m$

$$d \to \infty, x \to \infty$$

$$dd = \frac{dx}{2}$$

Therefore (6.21) becomes

$$\frac{f(m, o, T)}{n(m)} = \frac{J_d^*(m)}{2 \beta_d s(x^*)} \int_G^d \frac{dk}{n(x)}$$

(6.23)

Since

$$n(x) = n_1 \exp\left[-\frac{1}{kT} \left(\Phi(x) \right) \right] \geq n_1 \exp\left[-\frac{1}{kT} \left(\Phi(x) - \lambda(x-x^*)^2 \right) \right]$$

(4.58)

where

$$\lambda = \left[ -\frac{1}{kT} \Phi''(x^*) \right]^{1/2}$$

if one sets $-\lambda^2 = -\frac{1}{kT}(x-x^*)^2$ then (6.23) becomes

$$\frac{f(m, o, T)}{n(m)} = \frac{J_d^*(m) e^{-\lambda^2}}{2 \beta_d s(x^*) \sqrt{\pi}} \int_{(m-x^*)}^{x^*} e^{-\frac{k^2}{2}} dk$$

(6.24)

Since $m < x^*$, $(m - x^*) \lambda$ may be set to $-\infty$ while $G$ may be set to $+\infty$. This introduces virtually no error. Thus (6.24) becomes

$$\frac{f(m, o, T)}{n(m)} = \frac{J_d^*(m) \sqrt{\pi}}{2 \beta_d s(x^*) n(x^*) \lambda}$$

or

$$J_d^*(m) = \frac{2 \beta_d s(x^*) n(x^*) \lambda}{f(m, o, T) n(m) \sqrt{\pi}}$$

(6.25)

Similarly, it can be shown that

$$J_m^*(d) = \frac{f(0, d, o, T) \beta_d s(x^*) n(x^*) \lambda}{n(x^*) \sqrt{\pi}}$$

(6.26)

where

$$2d = x^* - m$$

(6.27)

$J_d^*(m)$ represents the flow of embryos (across the line $x^* = m + 2d$) parallel to the d axis, due to dimer impact only
(upon embryos of size \( x^* \)).

\( J^*_m(d) \) represents a similar vector flow (across \( x^* = m + 2d \)) due to monomer impact.

\( f(m, o, t) \) represents a non-equilibrium distribution of embryos which arise due to a net process of monomer impact. \( f(o, d, t) \) represents a similar distribution along the other boundary.

Note that \( f(m, d) \neq f(m + 2d) \) since nowhere has \( f(m, d) \) been summed over \( m + 2d = x \) and, even if it were, the form of \( f(m, d) \) is still unknown. This means that \( f(m, d) \) has meaning only with respect to a point on the \( m, d \) plane being the number of embryos of the size \( (m, d) \) at the time \( t \). \( n(m + 2d) \) has meaning only with respect to a line on the plane, each point of which contributes a quantity \( n(m, d) \) to \( n(m + 2d) \).

From the boundary conditions that the net flux vectors at \( m = 0 \) and \( d = 0 \) are parallel to these axes, expressions for \( \frac{f(o, d, t)}{n(2d)} \) and \( \frac{f(m, 0, t)}{n(m)} \) may be derived.

Thus (6.4) and (6.15) yield, at \( m = 0 \)

\[
\frac{\partial}{\partial m} \left[ \frac{f(m, d, t)}{n(x)} \right]_{d, m=0} = 0
\]

(6.28)

Therefore

\[
\left[ \frac{f(o, d, t)}{n(2d)} \right]_{d} = Q(d, t)
\]

(6.29)

Integrate (6.14) at constant \( m \):

\[
\int_{d_1}^{d} J_d(m, d, t) \, dd = \int_{d_1}^{d} \frac{\partial}{\partial d} \left[ \frac{f(m, d, t)}{n(x)} \right] \, dd = -\left[ \frac{f(m, d, t)}{n(x)} \right]_{m}
\]

(6.30)
Since \( m = 0 \)
\[
\int_{-d}^{d} \frac{J_d(0,d,t)}{\eta(\omega s(\omega)) n_d} \, d\omega = - \left[ \frac{f(0,d,t)}{n(2d)} \right]_1^d \tag{6.31}
\]

If \( J_d(0,d,t) \) is assumed to be independent of \( d \) (this is equivalent to assuming a quasi steady-state on the boundary) \((6.31)\) becomes
\[
\int_{-d}^{d} \frac{J_d(0,d,t)}{\eta(\omega s(\omega)) n_d} \, d\omega = - \frac{f(0,d,t)}{n(2d)} + \frac{f(0,1,t)}{n(2)} \tag{6.32}
\]

Therefore
\[
\frac{f(0,d,t)}{n(2d)} = 1 - \frac{J_d}{\beta_d} \int_{-d}^{d} \frac{d\omega}{\eta(\omega s(\omega)) n(2)} \tag{6.33}
\]

Note that as \( d \to \infty \), \( \frac{f(0,d,t)}{n(2d)} \to 0 \), and therefore
\[
J_d = \beta_d \int_{-d}^{d} \frac{d\omega}{\eta(\omega s(\omega)) n(2)} \tag{6.34}
\]

Similarly on the boundary \( d = 0 \), from (6.5) and (6.14)
\[
\frac{\partial}{\partial d} \left[ \frac{f(m,d,t)}{n(x)} \right]_{m, d=0} = 0 \tag{6.35}
\]

Therefore
\[
\frac{f(m,0,t)}{n(m)} = Q(m,t) \tag{6.36}
\]

From (6.15)
\[
\int_{m}^{M} \frac{J_m(m,d,t)}{n(x)s(x) \beta_m} \, dm = - \int_{1}^{m} \frac{\partial}{\partial m} \left[ \frac{f(m,d,t)}{n(x)} \right] \, dm \tag{6.37}
\]

Therefore at \( d = 0 \)
\[
\frac{f(m,0,t)}{n(m)} = 1 - \frac{J_m}{\beta_m} \int_{1}^{m} \frac{dm}{n(m)s(m)} \tag{6.38}
\]

or
\[
J_m = \beta_d \int_{0}^{\infty} \frac{dm}{n(m)s(m)} \tag{6.39}
\]

since
\[
\lim_{m \to \infty} \frac{f(m,1,t)}{n(m)} = 0
\]
The boundary conditions essentially imply that on the boundary, a one component distribution exists, at the same total pressure as the "two component" mixture of monomer and dimer.

One can see this by analogy with the one component steady state solution given by Equation (4.59).

5. Calculation of the Rate

The detailed physical mechanism of formation is not of direct interest and the vector scheme is used only to organize the counting process.

The total rate of flow across any line $x$ represents the flow through a given embryo size $x$. The line $x$, however, is not any line segment in the $(m,d)$ plane but that given by $x = m + 2d$ since only on this line do the "different" embryos correspond to the same physical entity of interest.* This considerably simplifies the analysis.

The critical rate is the rate of passage over the line $x = (m + 2d)^*$; this is the flux of physical interest.

To compute this flux, consider a line segment of $x^*, dL$ (Figure 37). If $J^*_m(d)$ and $J^*_d(m)$ are assumed constant over this line segment (which is assumed long enough to intersect an appreciable number of points $(m,d)$) the number of points intersected by $J^*_d(m)$ and $J^*_m(d)$ may be computed; multiplying these constant fluxes by the number of times they occur on

---

* The normal two-component case distinguishes all embryos, and flow across any line segment is physically significant.
CALCULATION OF THE TOTAL FLUX

FIGURE 37
dL and summing, an expression for \( J(x^*) \) is obtained over the segment dL:

\[
J(x^*)_{m,d} = n_m J^*_m(d) + n_d J^*_d(m)
\]  

(6.40)

where \( n_m \) is the number of m coordinates in dL and \( n_d \) each of which contribute \( J^*_m(d) \) and \( J^*_d(m) \) respectively to the flux over dL.

But

\[
n_m = dL \sin \theta = \frac{2}{\sqrt{5}} dL
\]

(6.41)

\[
n_d = dL \cos \theta = \frac{1}{\sqrt{5}} dL
\]

(6.42)

Therefore

\[
J(x^*)_{m,d} = \frac{dL}{\sqrt{5}} \left[ 2 J^*_m(d) + J^*_d(m) \right]
\]

(6.43)

The flux per unit length is given by

\[
\frac{\partial J(x^*)}{\partial L_{m,d}} = \frac{J_L(x^*)}{\frac{2}{\sqrt{5}} \sqrt{5}} = \frac{2 J^*_m(d) + J^*_d(m)}{\sqrt{5}}
\]

(6.44)

The total flux over \( x^* \), \( J(x^*) \), is given by

\[
J(x^*) = \int_0^L J_L(x^*) \, dl
\]

(6.45)

where \( K = \) total length of the line \( x^* = m + 2d \).

The variable of integration may be transformed from \( L \) to \( m \) since \( L = \frac{1}{2} \sqrt{x^*^2 + d^2} \) is the distance from the point \( m = 0 \), \( d = x^*/2 \) to the point \( (m, d) \).

Hence, if \( L = 0 \) then \( m = 0 \) and if \( L = K = \frac{x^*}{2} \) then \( m = x^* \).

(6.45) then reduces to

\[
J(x^*) = \int_0^{x^*} J_L(x^*) \frac{\sqrt{5}}{\varepsilon} \, dm = \int_0^{x^*} \left[ J^*_m(d) + \frac{J^*_d(m)}{\varepsilon} \right] \, dm
\]

(6.47)

Combination of (6.47), (6.25) and (6.26) yields

\[
J(x^*) = \frac{SC(x^*) n(x^*)}{\sqrt{\pi}} \int_0^{x^*} \left[ \frac{f(a, d, t)}{n(x^*)} \beta_m + \frac{f(m, a, t)}{2n(m)} \beta_d \right] \, dm
\]

(6.48)
Nowhere has the steady state approximation been explicitly used except at the boundaries, and even there, a true steady state was not necessary: only a very weak dependence on time. It is this weak dependence which is considered in \( J(x^*) \) (due to the presence of \( \frac{f(x,t)}{n(x)} \) and \( \frac{f(n,0,t)}{n(m)} \)).

This quasi-steady state situation arises from the fact that a peak integration has been performed (66f). If one considers the expression for the flux, Equation (4.45), then by integration together with (4.49) one obtains

\[
\frac{f(G)}{n(G)} = \left( - \int \frac{Tdx}{n(x) \infty} \right) G > x^* \quad (6.49)
\]

The flux as a function of time is schematically shown in Figure 38. The flux, \( I \), at early times, \( t_1 \), is nearly zero at \( x^* \). The function \( 1/n(x) \) is zero everywhere else and hence their product vanishes. \( \frac{f(G,t)}{n(G)} = 0 \), however, and the integral must be equal to unity: clearly impossible. When the flux increases, though not yet a steady state, the integral does not vanish and the peak integration will be valid. Note that \( I \) cannot change too sharply with \( x \) in order that it be possible to take it outside the integral sign.

\( J(x^*) \) is thus weakly time dependent - a quasi-steady state. It is a valid expression at times long enough so that the flux is not zero through \( x^* \) and not changing too rapidly with \( x \).

6. The Equilibrium Distribution of Embryos

In order to be able to compute the rate \( J(x^*) \) the quantity \( n(x) \), the equilibrium distribution of embryos in
VARIATION OF FLUX WITH TIME

FIGURE 38
the system must be calculated. This is most conveniently done by the method of Frenkel though it is realized that there is an approximation involved.*

Let $\Phi(T, p)$ be the thermodynamic potential of a system composed of a gaseous mixture of monomer and dimer molecules together with a distribution of liquid embryos whose size is measured in number of particles $x$.

Monomer and dimer in the gas phase satisfy some equilibrium relation due to the reaction

$$2M \rightleftharpoons D$$

The following notation will be employed:

- $m_0$ = number of monomers in gas phase at pressure $p_m$ with chemical potential/molecule equal to $\mu_m(p_m, T)$ where
  $$\mu_m = \mu_m^o(T) + kT \ln p_m$$  \hspace{1cm} (6.50)
- $d_0$ = number of dimers in gas phase at pressure $p_d$ with chemical potential/molecule equal to $\mu_d(p_d, T)$ where
  $$\mu_d = \mu_d^o(T) + kT \ln p_d$$  \hspace{1cm} (6.51)
- $p_T$ = total pressure $= p_m + p_d$
- $n(m + 2d) = n(x)$ = number of embryos of size $x$ in the equilibrium mixture.

- $\lambda_x$ = chemical potential of an embryo of size $x$.
  $$\lambda_x = x\lambda_L(T) + \alpha x^{3/2} \quad \text{(in the Frenkel approximation)}$$  \hspace{1cm} (6.52)

- $\lambda_L(T)$ = chemical potential per molecule of liquid under total pressure $p_T$ and temperature $T$.

The constraints on the system are

$$2\mu_m = \mu_d \quad \text{(or} \quad \kappa p = \frac{p_d}{p_m^2})$$  \hspace{1cm} (6.53)

*See Chapter IV, section 4.
and

\[ N_T = m_0 + 2d_0 + \sum_x \lambda(x) = \text{constant} \quad (6.54) \]

(where essentially \( 2 \lambda m = \lambda d \) is assumed.)

If the whole mixture is considered as a dilute solution of embryos in the gaseous solvent, the thermodynamic potential may be written

\[ \Phi(T, P) = m_0 \mu_m + d_0 \mu_d + \sum_x \left( x \lambda(x) + \alpha(x) x^{1/3} \right) \eta(x) + \kappa T \sum_x n_x \lambda(x) \eta(x) \quad (6.55) \]

where

\[ F = m_0 + d_0 + \sum_x \eta(x) = m_0 + d_0 \quad (6.56) \]

The condition of equilibrium is given by (4.17), subject to (6.53) and (6.54).

By the method of Lagrange multipliers (21b) one finds

\[ \eta(x) = F_{\exp} - \frac{1}{k_T} \left[ x \left( \lambda_L(P, T) - \mu_m(P_m, T) \right) + \alpha x^{1/3} \right] \quad (6.57) \]

The evaluation of \( \lambda_L(P, T) - \mu_m(P_m, T) \) is carried out in the following manner: for bulk liquid at its saturation pressure, \( P_0 \),

\[ \lambda_L(P_0, T) = \mu_q(P_0, T) \quad \text{chemical potential of gas phase (per molecule)} \quad (6.58) \]

By definition

\[ N \mu_q(P_0, T) = m_0 \mu_m(P_m, T) + d_0 \mu_d(P_d, T) \quad (6.59) \]

where \( N = m_0 + 2d_0 \), \( P_m^0 \) is the partial pressure of monomer over bulk liquid, and \( \mu_m(P_m^0, T) \) is the chemical potential of the monomer. (Note that \( P_0 = P_d^0 + P_m^0 \)).

From (6.59) and (6.53),

\[ \lambda_L(P_0, T) = \frac{m_0}{m_0 + 2d_0} \mu_m + \frac{d_0}{m_0 + 2d_0} \mu_d = \frac{m_0 \mu_m + 2d_0 \mu_d}{m_0 + 2d_0} \quad (6.60) \]

* There are no free energy of mixing terms for \( m_0 \) and \( d_0 \) since the \( \mu_m \) and \( \mu_d \) are expressed in terms of partial pressures.
Since the liquid is virtually incompressible,
\[ \lambda_L (P, T) \equiv \lambda_L (P, T) \]  
(6.61)

Therefore
\[ \lambda_L (P, T) \equiv M_m (P_m, T) \]
\[ \equiv M_m^0 (T) + \kappa T \ln P_m \]  
(6.62)

But
\[ M_m (P_m, T) = M_m^0 (T) + \kappa T \ln P_m \]  
(6.50)

Combining (6.50) and (6.62),
\[ \lambda_L (P, T) - M_m (P_m, T) = \lambda_L (P, T) - M_m^0 (T) - \kappa T \ln P_m \]  
(6.63)

and combining (6.63) with (6.62) the final expression is
\[ \lambda_L (P, T) - M_m (P_m, T) = \kappa T \ln \frac{P_T}{P_m} \]  
(6.64)

\( P_m \) can be eliminated as a variable in favor of \( P_{Total} \) in the following manner: assuming an ideal gas
\[ P_T V = (m_0 + d) k T \equiv F k T \]  
(6.65)

From (6.53)
\[ \nu_F = \frac{P_d}{P_m^2} \]

By definition
\[ P_T = P_m + P_d \]  
(6.66)

Combining (6.53), (6.65) and (6.66) when \( Kp \neq 0 \)
\[ P_m = \frac{1}{2 \nu_F} \left[ \sqrt{1+4Kp} - 1 \right] \]  
(6.67)

and
\[ n(x) = \frac{P_T}{K_T} \exp \left( \frac{-1}{K_T} \left[ x K_T \ln \frac{\sqrt{1+4Kp} - 1}{1+4Kp} + \alpha x^{2/3} \right] \right) \]  
(6.68)

When \( Kp = 0 \)
\[ P_m^0 = P_o , \quad P_m = P_T \]

and
\[ n(x) = \left( \frac{P_T}{K_T} \right) \exp \left( \frac{-1}{K_T} \left[ x K_T \ln \frac{P_m^0}{P_m} + \alpha x^{2/3} \right] \right) \]  
(6.69)
The critical nucleus size $x^*$ is gotten from

$$\frac{d}{dx} \left[ \frac{n(x)}{x^*} \right]_{x=x^*} = 0$$  \hspace{2cm} (6.70)$$

$$x^* = \frac{8}{2^{1/3}} \alpha^3 \left[ \frac{1}{\nu_T n \left( \frac{1+4Kp}{1+4Kp} - 1 \right)} \right]^{3/2} \quad Kp \neq 0$$  \hspace{2cm} (6.71)$$

$$\alpha = 4\pi \sigma \left( \frac{3\pi}{4\pi} \right)^{2/3}$$  \hspace{2cm} (6.72)$$

Thus, for $Kp \neq 0$

$$n(x^*) = \left( \frac{PV}{\nu_T} \right) \exp \left\{ -\frac{1}{\nu_T} \left[ \frac{4\alpha^3}{2^{1/3}} \left[ \frac{1}{\nu_T n \left( \frac{1+4Kp}{1+4Kp} - 1 \right)} \right]^{2} \right] \right\} \quad (6.73)$$

To complete the analysis

$$S(x^*) = \frac{\alpha}{6} x^{2/3}$$  \hspace{2cm} (6.74)$$

$$v_{x^*} = \left( \frac{\alpha}{3\nu_T} \right)^{1/2} x^{2/3}$$  \hspace{2cm} (6.75)$$

It is of interest to examine the limiting forms of $n(x)$ for large and small $Kp$:

**When $Kp = 0$ (no dimer)**

$$n(x) = \left( \frac{PV}{\nu_T} \right) \exp \left\{ -\frac{1}{\nu_T} \left[ x \nu_T \ln \left( \frac{P}{P_0} \right) + \alpha x^{2/3} \right] \right\}$$  \hspace{2cm} (6.76)$$

**When $Kp < 0$ (very small % dimer, so that $4Kp << 1$)**

$$(1+4PKp)^{1/2} \approx 1+4PKp$$  \hspace{2cm} (6.77)$$

and $n(x)$ is unaltered.

**When $Kp >> 0$ (small % monomer, $4Kp >> 1$)**

$$(1+4PKp)^{1/2} \approx (4PKp)^{1/2}$$  \hspace{2cm} (6.78)$$

$$n(x) = \left( \frac{PV}{\nu_T} \right) \exp \left\{ -\frac{1}{\nu_T} \left[ \nu_T \ln \left( \frac{P_0}{P} \right)^{1/2} + \alpha x^{2/3} \right] \right\}$$  \hspace{2cm} (6.79)$$

7. **Results**

The calculation of $J(x^*)$ for various ratios of monomer to dimer has been carried out for ethanol at 273\textdegree K and a
The integrals involved in the quantities \( \frac{f_0(x,t)}{n(x,t)} \) and \( \frac{f(m_0,t)}{n(m)} \) were evaluated numerically in the manner described in Chapter V. The data are given in Table 18.

The rate \( J(x) \) is given as a function of the percentage of dimer in the gaseous mixture (Table 19) and is illustrated in Figure 39.

The striking dependence of the rate upon the dimer concentration is clearly indicated: as the percentage of dimer increases, the rate drops, quite contrary to our a priori beliefs and in contrast with the results of Frisch and Willis!

If one examines the calculation of the latter authors carefully, it is clear that their analysis is not applicable to the situation envisioned here: a monomer-dimer equilibrium in the gas phase.

These authors set up the differential difference equation for the collisional flux through an embryo size when both single molecules and embryos of size 2 can collide with any embryo.

They write for this flux

\[
J = \alpha(x-1)f(x-1) - \beta(x)f(x) - \eta(x)f(x) + \frac{1}{2}(x-1)f(x-1)
\]

and the final result is expressed in the form

\[ (6.80) \]

* It was not feasible to use methanol as the example since the association cannot be regarded solely as monomer-dimer (79). The supersaturation refers to total pressure over total equilibrium vapor pressure of bulk liquid.
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**TABLE 19**

Calculation of the Total Rate

\[
K_p = 50 \times 10^{-6} \text{(97.7\% dimer)} \quad K_p = 10^{-1} \times 10^{-\text{6\% dimer}} \quad K_p = 5 \times 10^{-4} \times 10^{-\text{6\% dimer}}
\]

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\(J(x^*) = 2.3x10^{-24}\) \quad \(J(x^*) = 5.5x10^{-22}\) \quad \(J(x^*) = 2.71x10^{16}\)
\[ J^* = \frac{J_{\text{BDZ}}}{[1 + \frac{1}{6} \beta_{12}]} \]  

(6.81)

\[ \beta_{12} = \frac{S_i \eta(i)}{S_i \eta(i)} \]

where \( J_{\text{BDZ}} \) is the usual steady-state monomer solution \( J^* \) (Equation 4.59).

Clearly, until the factor \( 1 + \frac{1}{6} \beta_{12} \) can compete with the exponential in \( J_{\text{BDZ}} \) (equal to \( \exp \left( -\frac{\Delta G^+}{kT} \right) \)), the monomer solution will obtain. This competition will occur if \( \eta(2) \gg \eta(1) \) and thus an appreciable effect on the rate should only occur when the "dimer" concentration is very high. Furthermore, the rate should increase.

The resolution of this difficulty lies in the fact pointed out earlier: there is a meaningful difference between the perturbation of the flux due to collisions between embryos and the alteration of the flux due to the existence of association in the gas phase.

This difference occurs due to the thermodynamics of the situation. Frisch and Willis assert an appreciable effect will occur in the system if

\[ \eta(2) \gg \eta(1) \]

\( n(x) \), however, is given by

\[ n(x) = N_0 \exp \left( -\frac{1}{kT} \left[ xkT \ln \frac{P_0}{P} + x^{2/3} \right] \right) \]

and \( n(2) \) cannot become larger than \( n(1) \)!

* In the terminology of the authors.
These authors have considered the modification in the rate theory only and assumed that the original thermodynamic analysis would be valid! For the case of the perturbation by "embryo of size 2" collisions, this is true. When one asserts that association is occurring,* then the constraint

\[ 2\mu_m = \mu_d \]  

(6.53)
is required.** This condition completely alters the thermodynamic analysis and, in particular, as the concentration of dimer increases, the vapor phase is very strongly stabilized (the barrier \( \Delta\Phi(x^*) \) rises sharply) and the rate falls off quite rapidly.

In the situation for which (6.53) holds it is possible to have more dimers than monomers yet maintain the requirement that

\[ n(2^* < n(1) \]
since "embryos of size 2" and "dimers" are distinguishable. The quantity \( n(2) \) refers to entities derived by a fluctuation process over and above the number of dimers present.***

In order to see more clearly the effect of the kinetic versus the thermodynamic effects the calculation of the rate has been carried out as if for a pure one-component system

* Meaning the species can be identified.

** This implies \( K_p = \frac{P_d}{P_m^2} \).

*** On could also argue that the embryo distribution is not correctly given except at the nucleus size since the only thermodynamic entities present in the system are the monomer, dimer and nucleus.
except that the molecular weight has been replaced by a mean molecular weight, $\langle M \rangle$, weighted according to the mole fraction of monomer and dimer.

Thus, if $M$ is the molecular weight of the monomer,

$$\langle M \rangle \equiv x_m M + x_d (2M)$$  \hspace{1cm} (6.83)

where $x_m =$ mole fraction of monomer

$\langle M \rangle =$ mean molecular weight.

and, since $x_m + x_d = 1$, (6.83) may be written

$$\langle M \rangle = M (2-x_m) = M \gamma$$  \hspace{1cm} (6.84)

The calculation has been carried out for ethanol at the same temperature and supersaturation. The critical rate is given by

$$\Gamma^* = 1.13 \times 10^{-29} \gamma^{1/4} \exp(-32.66 \gamma^2)$$  \hspace{1cm} (6.85)

and is shown as the dashed curve in Figure 39.

Clearly, the effect is quite pronounced; in particular, almost the entire effect is due to the thermodynamics rather than the kinetics. The deviations of the kinetic analysis from the pure monomer or pure dimer system are understandable in the following manner: when one allows a small amount of dimer to be present in the system, the number of paths to the critical nucleus size is greatly increased while the thermodynamics is nearly unaltered. As more dimer is added, the thermodynamic effect predominates. Hence, the small peak at about 5% dimer. When the system is nearly all dimer, a similar effect occurs and the sharp drop in rate going from 95% to 100% dimer is observed.
8. Conclusions

The attempt to correlate the Volmer-Flood experiments with a modified theory was not successful. The magnitudes involved (% dimer necessary to cause an effect) are far beyond the experimental observations on the various vapors (88). The direction, however, is correct: a higher percentage of dimer means a lower rate, \( J^* \), and a higher critical supersaturation ratio. Methanol, it will be recalled, gave a higher value of \( S_{\text{critical}} \) than calculated on the basis of pure monomer.

The fact that the purely thermodynamic analysis (with the mean molecular weight concept) yields results closely paralleling the more accurate solution suggests that this will be a convenient approximate method for handling polymer formation in nucleation. It was not extended to treat methanol as there is only one experimental point to be checked (the critical supersaturation ratio) and at least two parameters, the equilibrium constants for dimer and (probably) tetramer formation, are involved. It should be noted that even small percentages of very high order polymers could exert an appreciable effect.
VII. GENERAL SUMMARY AND CONCLUSIONS

It was the purpose of this research to examine the validity of the experimental basis of the Becker-Döring theory of nucleation; to effect this, a careful examination of the usual experimental technique was carried out and a modified cloud chamber designed and constructed. The operating characteristics of the chamber were examined to insure that the modification in design did not introduce new errors in place of the ones which the chamber was designed to minimize. In particular, the expansion was found to be adiabatic and there was no appreciable lag in the appearance of condensate on the time scale involved in these experiments.

The experimental findings, though few in number, do not confirm the results of Volmer and Flood on the critical supersaturation ratio for the spontaneous nucleation of water vapor though they are in agreement with the classical results of C.T.R. Wilson and the more recent findings of G.M. Pound.

In an attempt to correlate all the experimental data, an hypothesis has been advanced which asserts, in effect, that the lack of agreement between the various investigators results from the failure of earlier workers to remove completely, by means of an electric field, the ever-present ions from the chamber. The associated question of which of the various criteria employed to define the appearance of condensate is correct must be examined in the light of the degree of purity of the carrier gas in any given experimental
situation. The various criteria could easily correspond to varying degrees of purity. Closely connected with this problem is the problem of the growth of the nuclei to observable droplets where the usual assumption of a 1:1 correspondence is an important part of the theoretical criterion for condensation.

Considerable experimental difficulty was experienced in obtaining, consistently, a sufficiently pure carrier gas for use in these experiments. Clearly, unless purity can be guaranteed the experiments are not capable of interpretation in terms of the theory of spontaneous nucleation. Formally, of course, ion removal is simply another form of purification though this was not the problem encountered with the erratic cleaning lines previously described.

An investigation of the influence of polymer formation in the vapor phase upon the gaseous nucleation process was carried out since the vapors under consideration in the experiments of Volmer and Flood are capable of vapor phase association. For the experimentally observed degrees of association in the lower alcohols, the effect is quite negligible though any appreciable percentage of polymer in the vapor exerts a tremendous stabilizing influence on the vapor phase.

The absence of relaxation effects in the attainment of steady state nucleation was confirmed.

On the basis of the experimental findings, one must conclude that the quantitative B.D.Z. theory is incorrect as
applied. There are several factors which enter into the comparison of theory and experiment and consequently several possibilities for error in the analysis. One cannot say that any given part of the formalism is incorrect. The nature of the criticism of the basic thermodynamics, particularly with regard to the magnitude of the surface tension, makes this appear to be the most reasonable point of departure in a more refined analysis; Reiss has indicated a statistical mechanical approach to the problem (see Appendix I).
APPENDIX I

THE STATISTICAL THEORY OF NUCLEATION

1. Outline of the Theory

The severe conceptual difficulties of the quasi-thermo-dynamic theory of nucleation led Reiss (66d) to attempt a more rigorous treatment of the problem. In particular, the equilibrium aspect of the theory was considered from the point of view of statistical mechanics.

At the outset, it was recognized that a truly rigorous treatment could not lead to the existence of metastable states, but would lead to the phenomenon of phase separation (as in the theory of Mayer) since the system in which two stable phases exist has a lower Gibbs free energy than the corresponding single phase metastable system (20a). It was therefore necessary to introduce some constraint into the system which would force it to remain metastable; since, for a supersaturated vapor, the metastability is made evident by its remaining gaseous, Reiss chose to constrain the system in this fashion.

The fundamental problem in the statistical mechanics of cooperative systems is the evaluation of that part of the phase integral known as the configuration integral (20b)

\[
\Omega = \int \ldots \int_V \exp \left( -\frac{1}{kT} \left[ U(q_1, \ldots, q_n) \right] \right) (dw)^n \quad (A.1)
\]
from the phase integral all the thermodynamic functions may be derived. In particular, the pressure is given by (20c)

\[ p = \kappa T \left( \frac{\partial \ln \Omega}{\partial V} \right)_T \]  

(A.2)

For an ideal gas $\Omega = V^N$ (since $\mathcal{U} = 0$) and hence

\[ pV = NkT \]  

(A.3)

For this reason, Reiss chose to impose the constraint in the form

\[ \Omega = V^N \]  

(A.4)

without requiring $\mathcal{U} = 0$. The very fact that condensation does occur implies some sort of interaction.

The evaluation of $\Omega$ was carried out by means of a cell method of calculation in which one assumes the configuration space to be divided up into cells and approximates the integral over the whole space by integrals over the cells.

The distribution of cells of size $x$ (having $x$ molecules in the cell), was found to be

\[ n(x) = \frac{\lambda^x}{x!} e^{\gamma x} \exp \left[ - \frac{\langle \omega(x) \rangle_{\Omega}}{\kappa T} \right] \]  

(A.5)

where $\lambda$ and $\gamma$ are Lagrange multipliers on the conservation of particles and volume, $\langle \omega(x) \rangle_{\Omega}$ is a mutual potential energy of $x$ particles in a cell including interactions between particles in neighboring cells.*

The conservation conditions are

\[ \sum_x n(x) = N/g \]  

(A.6a)

* A similar result was obtained independently by Katsura and Fujita (39) though intercell interaction was ignored.
\( \sum_{\alpha} n(\alpha) x = N \)  \hspace{1cm} (A.6b)

and \( \lambda \) and \( \gamma \) are determined from these constraints.

If \( \langle \omega \rangle_{\omega} \) is zero, as for an ideal gas,

\begin{equation}
\langle \omega \rangle_{\text{id}} = \frac{\lambda_{\text{id}} \gamma_{\text{id}}^{x}}{x!} \tag{A.7}
\end{equation}

and the conservation conditions lead directly to

\begin{equation}
\gamma_{\text{id}} = q \quad \text{and} \quad \lambda_{\text{id}} = \frac{N}{q} e^{-q} \tag{A.8}
\end{equation}

Therefore

\begin{equation}
\Omega_{\text{id}} = \frac{N}{q} e^{-q} \left( \frac{q^{x}}{x!} \right) \tag{A.9}
\end{equation}

\( \Omega \) is wholly determined by \( \lambda \) and \( \gamma \). Reiss chose them for the non-ideal system to be those given for an ideal gas. (This insures that (A.4) will be satisfied). Hence

\begin{equation}
\Omega = \frac{N}{q} e^{-q} \left( \frac{q^{x}}{x!} \right) \exp \left[ - \frac{\langle \omega \rangle_{\omega}}{\sqrt{x} \Gamma} \right] \tag{A.10}
\end{equation}

This \( n(x) \), however, cannot satisfy the conservation conditions as the series (A.6) diverge. To eliminate this, it is necessary to cut off these series at some value \( h \). Thus

\begin{equation}
\sum_{0}^{h} \frac{N}{q} e^{-q} \frac{q^{x}}{x!} \exp \left[ - \frac{\langle \omega \rangle_{\omega}}{\sqrt{x} \Gamma} \right] = \frac{N}{q} \tag{A.11}
\end{equation}

\begin{equation}
\sum_{0}^{h} x \frac{N}{q} e^{-q} \frac{q^{x}}{x!} \exp \left[ - \frac{\langle \omega \rangle_{\omega}}{\sqrt{x} \Gamma} \right] = N \tag{A.12}
\end{equation}

Examination of the extremals of the distribution function \( n(x) \) (in which \( x! \) was approximated by Stirling's formula) revealed that two extrema existed: a most probable value at

\begin{equation}
x_{t} = q \tag{A.13}
\end{equation}
and a second (least probable (85)) defined by

\[-kT \ln \frac{x^*}{g} = \left[ \frac{d}{dx} \langle w(x) \rangle_{av} \right]_{x=x^*} \quad (A.14)\]

It was shown that cells of size \(x < x^*\) were more likely to decay, those of \(x > x^*\) more likely to grow. The size \(x^*\) was then identified as the analogue of the classical nucleus and for internal consistency, it was demanded that

\[x^* = h\quad (A.15)\]

By means of an inequality argument, it was shown that \(h\) increases more rapidly than \(x^*\) with \(g\) and hence there was a maximum size of cell, \(T (= gv)\), defined.

Finally an attempt was made to compute the exponent of \(n(x)\) from the quasi-thermodynamic arguments of the Einstein fluctuation theory.

The formalism of the rate theory was left unaltered.

2. Criticism of the Theory

In attempting to carry out a numerical investigation of the theory, certain difficulties were noted in the discussion.

The original investigation was concerned with the possibility of obtaining a consistent set of variables, \(g\) and \(h\), such that (A.4), (A.6a), (A.14) and (A.15) are satisfied (with \(n(x)\) given by (A.10)) with the tacit assumption that if one satisfied the conservation condition (A.6a), then (A.6b) would also be satisfied. This implies that

\[g \sum_0^h n(x) = \sum_0^h x n(x)\quad (A.16)\]
(so that the average value of $x$ over the distribution is the same as the most probable value)*.

By direct substitution of (A.10) into (A.16), one obtains

$$
\sum_{x=0}^{b} \frac{g^{x-1}}{(x-1)!} \exp \left[ - \frac{\langle w(x) \rangle_{aw}}{\kappa T} \right] = \sum_{x=0}^{b} \frac{g^{x}}{x!} \exp \left[ - \frac{\langle w(x) \rangle_{aw}}{\kappa T} \right]
$$

or

$$
\sum_{x=0}^{b} \frac{g^{x}}{x!} \exp \left[ - \frac{\langle w(x) \rangle_{aw}}{\kappa T} \right] = \sum_{x=0}^{b} \frac{g^{x}}{x!} \exp \left[ - \frac{\langle w(x) \rangle_{aw}}{\kappa T} \right]
$$

(A.17)

For the crude $\langle w(x) \rangle_{aw}$ chosen** this did not hold***.

Accordingly, an investigation was undertaken of the interrelationship of $\lambda$, $\gamma$, $g$, $h$, and $x$*. In particular, solutions of the set of equations

$$
\Omega = \mathbf{V}^N = \left( \frac{N}{g} \right)! n! (gv)^N \mathbf{e}^{N/2} \prod_{x} \left[ \frac{\exp \left[ - \frac{\langle w(x) \rangle_{aw}}{\kappa T} \right]}{x! n(x)} \right]^{n(x)}
$$

(A.18)

together with (A.6a), (A.6b), (A.14), (A.15), and (A.5)

were sought.

Substitution of (A.5) into (A.18) produces the requirement that

$$
\lambda_{crit} = \left( \frac{N}{g} \right) \left( \frac{g}{\gamma e} \right)^9
$$

(A.19)

* As will be seen below this is not true. This is an indication of the importance of the fluctuations!

** See section 3.

*** In this connection, it should be noted that the use of Stirling's approximation for $x!$ is not permissible due to the smallness of $x$ and the conservation conditions must be expressed as sums; conversion to integral conditions is invalid. This is consistent with viewing $x$ as a discrete parameter.
(A.5), (A.6a), and (A.6b) yield
\[ \sum_0^\infty (q-x) \frac{h^x}{x!} \exp - \left[ \frac{\langle w(x) \rangle_u}{\kappa T} \right] = 0 \] (A.20)
while (A.14) and (A.15) reduce to*
\[ \lambda = h \exp \left[ \frac{\omega(h)}{\kappa T} + \frac{1}{2h} \right]; \quad \omega(h) = \left[ \frac{d}{dx} \langle w(x) \rangle_u \right]_{x=h} \] (A.21)
The combination of (A.20) and (A.21) yields
\[ \sum_0^\infty \frac{(q-x)}{x!} h^x \exp - \frac{1}{\kappa T} \left[ -x \omega'(h) + \langle w(x) \rangle_u - \frac{x \kappa T}{2h} \right] = 0 \] (A.22)
For a given value of h, (which should be an integer) a value of g may be derived. Then, from (A.6a) and (A.6b) a value of \( \lambda \) may be computed. From (A.19) a value of \( \lambda \) may also be computed and the two compared. When they are equal, the desired set of g, h, \( \lambda \), \( \gamma \), and \( x^* \) will have been found. This has been carried out for a particular approximation to \( \langle w(x) \rangle_u \).

3. Calculation of \( \langle w(x) \rangle_u \)

It must be recognized at the outset that a direct calculation of \( \langle w(x) \rangle_u \) is not feasible. Accordingly, an approximation must be sought.

A reasonably tractable one would seem to be given by the Lennard-Jones-Devonshire theory of compressed gases (20d). In this lattice model, valid for highly compressed gases, the determining parameter (aside from the fundamental constants

* Here we must assume Stirling's approximation for \( x! \) but we choose the more exact form
\[ x! \approx e^{-x} x^x (2\pi x)^{1/2} \]
In the derivative, we do not make too great an error.
in the intermolecular potential) is the density.

The particles are considered to be fixed in a face-centered cubic lattice and a smoothed average potential \( w(r) \) for a particle with 12 nearest neighbors is computed. Thus

\[
w(r) = \frac{2}{2} \int e \left\{ (r^2 + 4a^2 - 2ar \cos \phi)^2 \right\} \sin \theta \, d\theta
\]

(A.23)

Restricting our consideration to the value of \( w(r) \) at the center of the cell defined by the 12 nearest neighbors,

\[
w(0) = \frac{1}{2} \left\{ \sum \left[ -4 \left( \frac{1}{a} \right)^6 + 2 \left( \frac{1}{a} \right)^{12} \right] \right\}
\]

(A.24)

In terms of the nearest neighbor distance, since there are 2 molecules per unit cell, the volume per molecule, \( V_m \), is given by

\[
V_m = \frac{V_{cell}}{4} = \frac{a^3}{\sqrt{2}}
\]

(A.25)

For the cells under consideration, the average volume per molecule is given by

\[
V_m = \frac{\pi}{\chi}
\]

(A.26)

Hence, equating (A.25) and (A.26) yields \( w(0) \) for these cells and hence \( w(0) \).

The energy in the cell \( \Upsilon \) is then approximately

\[
\frac{1}{2} \times w(0)
\]

(A.27)

(Where the factor \( \frac{1}{2} \) avoids double counting). The final result is

\[
\langle w(\Upsilon) \rangle_{aw} \approx \frac{1}{2} \times w(0) = \frac{1}{2} \left\{ \sum \left[ -24 \times \left( \frac{1}{\pi 12} \right)^2 + 12 \left( \frac{1}{\pi 12} \right)^{12} \right] \right\}
\]

(A.28)

The quantity \( \langle w(\Upsilon) \rangle_{aw} \) is really a free energy of charging; since an energy approximation is being used, an error is introduced. \( w(0) \) is a maximum (negative) value of \( w \) and the
entropy of charging is essentially a negative quantity; hence from

\[ \Delta F = \Delta E - T \Delta S \]  

(A.29)

it is expected that some compensation of the energy error will be obtained by omitting the entropy factor.

As to the use of the Lennard-Jones-Devonshire theory itself, one asserts that cells with \( x \) particles have approximately the energy of \( x \) particles in a bulk fluid of density \( \frac{\rho}{x} \). In this manner, the interactions across the boundary of the cell \( \tau \) are included but with cells of equal density. Since, however, \( n(x) \ll n(x-1) \) it is more likely that surrounding cells will have a lower density and hence, each particle in \( \tau \) will not have 12 neighbors. A uniform density has been assumed in the cell \( \tau \) with no transition region at the boundaries. Probably, the density in the middle of the cell will be higher than at the edge and, approximately, the extra energy due to assuming each particle has 12 near neighbors may compensate for the fact that the density assumed is too low. Schematically,

\[ \begin{array}{c}
\text{Actual density} \\
\frac{\tau}{x}
\end{array} \]

The use of \( \frac{1}{2} (n)[n(o)] \) for \( \langle w(x) \rangle_{00} \) is not as severe an approximation as would appear initially.

4. Results

The calculations were made for \( N_2 \) at 76.81°K with a supersaturation of 2.718 (\( p = 1943.6 \) mm).
For $N_2 (20e)$

$$\Lambda^* = 1.59 \times 10^{-15} \text{ ergs/molecule}$$

$$V^* = r V_A = 5.127 \times 10^{-23} \text{ cc}$$

$$\langle \omega \rangle_{\Omega} = - \left[ \left( \frac{x}{q^2} \right)^3 \right] \left[ 2.3524 \times 10^{-3} \right] + \left[ \left( \frac{x}{q^2} \right)^2 \right] \left[ 1.8441 \times 10^{-7} \right]$$

The results are summarized in Table A1.

The deviation of $\Omega$ from $V^N$ can be expressed as

$$\Phi = \frac{\ln \omega - N \ln v}{V} = \frac{1}{3} \ln \left( \frac{V}{N^3} \right) + \ln \left( \frac{g}{\xi^2} \right)$$

(A.30)

$$= \frac{1}{3} \ln \left( \frac{\lambda \xi}{\lambda} \right)$$

(A.31)

A plot of $\Phi$ vs $g$ is shown in Figure A1.

It is seen that $\Phi$ tends toward zero for large values of $g$ and increases quite sharply for small values. Only in the limit of $g \to \infty$ will $\Omega = V^N$. As the cell size becomes very small, the deviation from ideal gas behavior becomes quite striking! (As $g \to 0$, $\Phi \to \infty$).

One interesting point is that $h$ varies linearly with $g$ (Figure A2). This is not in conflict with the inequality argument of Reiss as this argument is valid only when $\lambda$ and $\gamma$ are identified with $\lambda_{id}$ and $\gamma_{id}$. It is not meaningful with respect to the present development.

Since no finite values of $\lambda$, $g$, $h$, $\gamma$, and $x^*$ will satisfy all the required relations, it is apparent that some modification must be made. The modification of the cutoff at the minimum would be not desirable as it represents a sort of critical point for cells. A more reasonable modification would seem to be in the condition on $\Omega$. If the gas is ideal $\Omega = V^N$. The gas is not really ideal, but slightly
TABLE A1

The Deviation of \( \Omega \) From Ideality

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<th>( h )</th>
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<td>390.92</td>
<td>1.0220</td>
<td>3.598</td>
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</table>
Figure A1
imperfect and from the theory of slightly imperfect gases, it can be shown (20f) that

$$\ln \Omega_{\text{eff}} = N \ln \sqrt{\frac{N^2 B_m(T)}{V}}$$

(A.32)

where $B_m(T)$ is the molecular 2nd virial coefficient.

For $N_2$ at $76.81^\circ \text{K}$, $B(T) = N B_m(T) = -0.2575$ liter/mole. (87)

$$\Phi = \frac{\ln \Omega_{\text{eff}} - N \ln V}{N}$$

(A.33)

$$= 0.117 \text{ at } 1943.1 \text{ mm.}$$

It can be seen from Figure A1 that such a value of $\Phi$ would require a very small value of $g$. The consequences of a $g < 1$ lead to a quite interesting result in the rate theory. By analogy with the B, D, Z, theory, the rate varies as $\exp^{-\langle \omega(x) \rangle / kT}$. For very small values of $g$ the rate becomes independent of $g$. This is quite reasonable inasmuch as $g$ does not possess any real physical significance; it is merely an aid in the calculation. No physical process should depend upon this arbitrary calculational aid.

This work was not continued for reasons which will be indicated in the comments on the rate theory. Before leaving the equilibrium theory, one last point should be indicated.

Reiss attempted to show that the exponent in the distribution function $n(x)$ could be calculated from the Einstein fluctuation theory (within limits) from a thermodynamic calculation of the reversible work of formation of such a cell. A careful examination of the fluctuation theory reveals that it is inapplicable to this case.

The development of the fluctuation theory may be based
on the canonical distribution function (35). Let there be two
groups of states 1 and 2. The probability of the system being
in a state in group 1 is given by

$$P_i = \frac{\sum \epsilon_i e^{-\epsilon_i/kT}}{\sum \epsilon_i e^{-\epsilon_i/kT}} = \frac{\sum \epsilon_i e^{-\epsilon_i/kT}}{\sum \epsilon_i e^{-\epsilon_i/kT}}$$  \hspace{1cm} (A.34)

where \( \sum \epsilon_i \) means summing only over those \( \epsilon_i \) which correspond
to the system being in group 1. From \( F = -kT \ln \sum \epsilon_i e^{-\epsilon_i/kT} \)

$$P_i = \frac{e^{-F_i/kT}}{e^{-F/kT}} = e^{-\Delta F_i/kT}$$  \hspace{1cm} (A.35)

The relative probability of the system being in group 1 is
related to the free energy change required to go from any
state in the whole assembly to a state in group 1. When the
states of group 1 are such that they may also be regarded as
a system, then \( F_1 \) may be identified with the macroscopic thermo-
dynamic free energy and calculated in this manner. If not
then \( \Delta F_1 = (F_1 - F) \) must be calculated from the defining
partition functions.

Applied to fluctuations in a variable from its mean
value, this implies that the state to which the fluctuation
leads is macroscopically describable. Hence, the fluctuations
from the second state must be negligible. This is not true for
the density fluctuations considered by Reiss; the relative
fluctuation varies as \( 1/\sqrt{x} \) where \( x \), the number of particles in
the cell, is not a large number. (Note that Stirling's ap-
proximation had to be applied here, again inadmissible).

The formalism shows too that the fluctuation theory
leads not to the probability that a system is in a given
state (say a cell with a given number of particles) but rather to a division of possible states (that a cell has no more than a given number of particles) \((73b)\). There may be an appreciable difference between the total number of states with a given density and the total number whose density does not exceed a given value.

Reiss has noted too that \(n(x)\) can be derived from purely probabilistic considerations* and in this manner one gets quite exactly the number of cells with a given number of molecules (no more and more less). It is essentially a Poisson distribution.

5. The Kinetic Theory

Reiss attempted to follow the exact formalism of the B.D.Z. approach in setting up the rate theory except that the statistical mechanical \(n(x)\) was used. One considers impacts on the cell "wall", which is plane and has a well defined area, and a quite analogous equation to \((4.49)\) for the rate, \(I^*\), may be derived. In particular, the identification of the number of impacts on the wall of the cell, with

\[
\bar{\beta} = \frac{\eta}{\sqrt{2\pi m k T}} \quad (\eta = \text{condensation coefficient})
\]

may be made where \(p\) = pressure of supersaturated vapor.

If one considers the point, however, one is really not interested in the number of impacts on the wall but in the number of molecules landing in the given cell. If the embryos

---

* See also the calculation on density fluctuations by Frey \((25)\).
of the classical theory were cubes, \( \beta \) would be just this quantity because the embryos were assumed to have a liquid density: impact (assuming \( \gamma = 1 \)) meant it joined the embryo.

In this case there is no analogous property of \( x \) molecules in a cell to prevent a molecule, jumping from an adjacent cell, from jumping right through the given cell into the next neighbor. Even the nucleus does not possess the liquid density. The number of impacts on the wall is given correctly by \( \beta \) but this is not the number which remain in the cell long enough to be counted (say the time between molecular collisions) as a cell of size \((x+1)\).

The mean jump length of the molecule may be assumed, to a first approximation, to be determined by its local density which varies from cell to cell. On the average, most cells have 1 molecule and thus their density is correctly given by the gas density and \( \beta = \frac{p}{\sqrt{2\pi nm\lambda t}} \). This must be regarded as only a first approximation and the point must be investigated. The gases are not ideal!

When this was realized, the futility of further numerical work on the theory became apparent; the results are thus limited.

The formulation of the problem of the evaluation of the relation between \( \beta \) and the number of molecules remaining in a cell long enough to be counted is a problem for molecular theory. One must know the types of cells surrounding the given cell and the distribution, within each, of the particles.
Then, the problem of a jump of a given length from a given position correctly averaged might shed some light on the problem.

6. **Conclusion**

In conclusion, the following may be observed:

1. The equilibrium theory as originally proposed by Reiss is untenable but modification of the condition on $\alpha$ appears to be a reasonable solution of the difficulty.

2. The modifications necessary in the rate theory may be quite extensive.

Notice that no surface tension entered these considerations: the activation energy is brought into existence by variations in density between various parts of the system.
APPENDIX 2

The Vapor Pressure of Supercooled Water

The vapor pressure of supercooled water (mm.) as a function of temperature (°C) is given in Figure A3. The values were taken for $T > -15^\circ C$ from the Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Brooklyn, (1951) pg. 1928 and for $T < -15^\circ C$, from the Smithsonian Meteorological Tables (6th Revised Edition), Smithsonian Institute, Washington, pg. 351.
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ABSTRACT

It has been observed that a vapor need not condense when it is saturated and, in fact, it may be considerably supercooled (or overcompressed), the general phenomenon being known as supersaturation. At sufficiently high supersaturation, condensation does occur.

The kinetic process leading to the collapse of a supersaturated state is termed nucleation and one distinguishes two types of nucleation. Spontaneous, arising without external influence and foreign, initiated by some external agent (dust, ions, etc.)

For pure vapors, the theory of spontaneous nucleation developed by Becker and Doring predicted quite precisely the critical supersaturation ratios (the minimum ratio of pressure to equilibrium vapor pressure, at a given temperature, necessary to cause condensation) observed by Volmer and Flood for several substances. The relevant parameters, beside temperature and pressure, are the liquid molecular volume and the surface tension. The theory must extrapolate these macro-thermodynamic concepts into the molecular domain, however, in which region their validity may be seriously questioned. In particular, theoretical considerations of Tolman and Kirkwood and Buff indicate a dependence on curvature of the surface tension of significance in the size range encompassed by the nucleation theory. The Becker-Doring analysis takes
no account of this; the agreement with experiment is obtained using the macro surface tension of the fluid. Considerable criticism of the conceptual basis of the theory of nucleation has appeared as a consequence.

It was the purpose of this research to examine the validity of the experimental basis of the Becker-Doring Zeldowitch theory by careful measurement of the critical supersaturation ratio of water vapor. In the course of research, investigations were carried out on the influence of association in the vapor phase upon the nucleation process, steady-state approximation of the nucleation theory, and the statistical mechanical theory of nucleation as developed by Reiss.

The experimental determination of the critical supersaturation ratio of water was carried out using the standard technique, adiabatic expansion of the saturated vapor, except that an examination of previous cloud chamber techniques to effect this measurement showed the need for modification of the design of the instrument. In particular, the measurement of the point at which condensation occurred was made during the expansion rather than at the end. This was accomplished by observing the formation of condensate photographically by recording the output of a 1P21 photomultiplier tube mounted at right angles to the monitoring light beam and, simultaneously, photographically recording the motion of the piston producing the expansion using a stroboscopic open-flash technique. The
stroboscopic pulses were also picked up by the IP21 making possible the correlation between piston position and the appearance of scattering and, hence, the determination of the critical supersaturation ratio.

It was considered desirable to avoid the presence of liquid in the chamber and, consequently, the saturation and purification (removal of foreign nuclei) of a flowing gas stream had to be accomplished. The usual purification technique of repeated expansions to "rain out" dirt could not be employed. Considerable difficulty was encountered in purifying the carrier gas and the results are limited.

For condensation on ions, the data are essentially in agreement with those of other investigators. For spontaneous nucleation, the data are not in agreement with the results of Volmer and Flood (and the theory). They are, however, in accord with the results of Wilson and coworkers and the very recent work of Pound. At $258^\circ \pm 0.5$ K, $S_{critical} = 7.5 \pm 0.5$ using $N_2$ as the carrier gas; theory predicts $S_{critical} \approx 5$. Pound has recently confirmed these experimental results using $H_2$ as the carrier gas but finds a somewhat lower value using $N_2$; for $O_2$, the theoretical value is obtained.

It is possible to correlate the existing data on the following basis. Wilson, Andren, and Pound report that the critical supersaturation ratio is dependent upon the nature of the carrier gas. The data of Andren indicate that when a clearing field is applied to a region
by means of electrodes placed inside the chamber (such that field free spaces are allowed to exist) ion removal is not complete. The observed results probably represent heterogeneous nucleation on ions. Thus, the highest ratios obtained by Pound are correctly ascribed by him as due to the fewer number of ions which naturally occur in H₂ as compared to N₂ or O₂. In this research the highest values were obtained using N₂ indicating more efficient removal of ions than previously attained.

The decision as to what represents a valid criterion of condensation is subject to much uncertainty when complete ion removal cannot be guaranteed.

The failure of the experimental data to agree with the prediction of theory may be due to inherent failure of the theory or the error may lie in the application of the theory to the experiment. It is to be noted that even for the Volmer-Flood experiments agreement with theory was not universal. In particular, for methanol, there was a serious discrepancy. If one examines the substances investigated, it is found that most of them associate in the vapor phase. The simple theory, however, regards the vapor phase as composed solely of monomer units. The influence of vapor phase dimerization upon the nucleation process was therefore investigated to determine whether or not a correct application of the theory would yield significantly altered predictions.
The problem was considered, formally, to be one of black nucleation, a treatment of which had been given by Reiss for the general case. The concept of the embryo plane in which liquid embryos of varying compositions (of monomer and dimer) are represented by lattice points, proves invaluable for the systematization of the molecular mechanisms leading to critical nuclei. The problem is greatly simplified when one chooses not to regard the monomer and dimer as distinguishable in the liquid phase. In this case, the critical nucleus size is represented on the plane by a line, the ordinate and abscissa representing the number of monomer and dimer additions making up a particular embryo. One can define vector flows in the plane representing monomer and dimer impact upon an embryo and compute a total flux through the critical nucleus size by integration of the net flow over all points on the line representing the critical nuclei. The boundary conditions do not permit any net flow over the boundaries of the embryo plane (at \( m = 0 \) and \( \varnothing = 0 \)) and require vanishing fluxes as \( m \) and \( \varnothing \) tend toward infinity. If one further demands that the number of embryos of size 1 and 2 are fixed at their equilibrium values, the problem is completely defined.

The calculations, carried out for ethanol at 273°K and a supersaturation ratio of 3, indicate an appreciable effect on the rate by a relatively small percentage of dimer in the vapor phase, tending to increase the critical
supersaturation ratio. Though the effect is qualitatively correct, the magnitude of dimer concentration necessary to account for the data on methanol is experimentally unrealistic.

To compare the relative effects of the kinetic and thermodynamic modifications necessary in the theory, the simple monomer analysis of Becker-Doring-Zeldowitch was used except that the molecular weight was replaced by an average (weighted according to the mole fraction of dimer and monomer). The effect appears to be almost wholly thermodynamic, the association reaction conferring great stability upon the vapor phase.

Frisch and Willis reported that there should be little or no influence on the rate due to dimerization; any effect should tend to lower the critical supersaturation ratio. The error in their analysis was traced to a neglect of the constraint in the thermodynamic analysis which relates to the condition of equilibrium in a chemical reaction. Their results apply strictly to the perturbation of the rate due to collisions involving embryos of size 2 and not to the influence of vapor phase dimerization.

Another possible source of error, pointed out by Kantrowitz, was the use of a steady-state approximation in the simple theory. He gave a very approximate solution of the relevant partial differential equation (into which he had incorrectly incorporated certain correction terms).
Collins derived a much improved solution valid in the region of the critical nucleus.

It was desirable to test the error incurred by specifying the solution to this region. Due to the nature of the equation, an approximation scheme had to be employed. A technique developed by Reiss proved useful. One assumes, essentially, that the flux in the region is a function only of the time. Proper selection of boundary conditions defines the problem completely.

The calculations were carried out for N₂ at 76.81⁰K and various supersaturations. The results indicate no appreciable transient and compare quite well with the more exact solution of Collins in the region of the critical nucleus.

Finally, an attempt was made to obtain numerical predictions of the critical supersaturation ratio of N₂ using the statistical mechanical theory developed by Reiss. Before much work had been done, however, a serious defect in the kinetic formulation of the theory, involving the identification of the number of impacts on an embryo leading to growth of the embryo, was discovered. The work was discontinued.
BIOGRAPHY

Howard M. Saltsburg, son of Morris and Rose Saltsburg, was born September 12, 1928 in the City of New York. He was educated in the public schools of that city and received the B.S. degree from the City College of New York. He entered Boston University, February 1950, as a research assistant in the Department of Chemistry and continued in this capacity until June 1951. At that time, he joined the Cloud Physics Group of the Air Force Cambridge Research Center and held a position as chemist until July 1954. He then accepted a postdoctoral fellowship in the Chemistry Department at the University of Rochester.