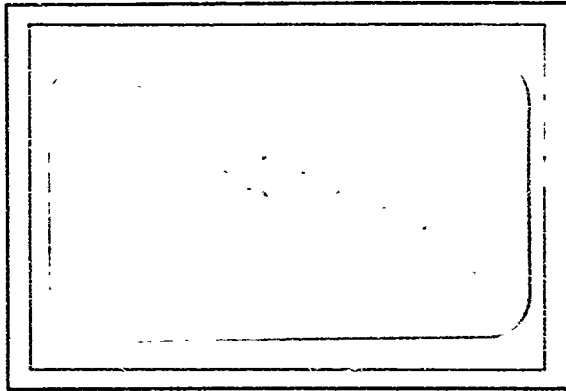


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THE KINETICS OF EVOLUTION OF  
WATER VAPOR CLUSTERS IN AIR

A. A. Pouring\*

December 1975

Report E.W. #3-74

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|---|-----------------------|---|
| 1. REPORT NUMBER<br>USNA-E&W #3-74  | 2. GOVT ACCESSION NO. | 3. REPORT'S CATALOG NUMBER<br><b>(9)</b>  |
| 4. TITLE (and Subtitle)<br><b>(6)</b> The Kinetics of Evolution of Water Vapor Clusters in Air.   |                       | 5. DATE OF REPORT & PERIOD COVERED<br>Final Report, 1964- <b>(1975)</b>           |
| 7. AUTHOR(s)<br><b>(10)</b> A. A. POURING   |                       | 8. CONTRACT OR GRANT NUMBER(s)  |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>United States Naval Academy<br>Aerospace Engineering Department<br>Annapolis, Maryland 21402   |                       | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS<br><b>(12)</b> 140 p. |
| 11. CONTROLLING OFFICE NAME AND ADDRESS<br>United States Naval Academy<br>Annapolis, Maryland 21402<br><b>(11)</b>  |                       | 12. REPORT DATE<br>December-1975  |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)<br><b>(14)</b> FW-3-74  |                       | 13. NUMBER OF PAGES<br>134  |
|   |                       | 15. SECURITY CLASS. (of this report)<br>Unclassified                              |
| 16. DISTRIBUTION STATEMENT (of this Report)<br><br>Distribution Unlimited   |                       | 18a. DECLASSIFICATION/DOWNGRADING SCHEDULE<br>N/A                                 |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  |                       |   |
| 19. SUPPLEMENTARY NOTES<br>Available in DDC   |                       |   |
| 20. KEY WORDS (Continue on reverse side if necessary and identify by block number)<br>Water Vapor                      Supersaturated                      Equilibrium<br>Clusters                              Metastable<br>Nucleation                              Undersaturated<br>Condensation                              Expansion<br>Nonequilibrium                              Supersonic   |                       |   |
| 21. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>The kinetic theory of cluster formation in a condensing gas proposed by Buckle <sup>(12)</sup> attempts to calculate the course of homogeneous condensation from molecular rather than thermodynamic precepts. Here it is applied to the rapid nonequilibrium expansion of atmospheric water vapor in air. A method is established for demonstrating the validity of this theory, originally proposed for a mono-molecular gas, in the case of a complicated species such as water vapor. Cluster conditions in the temperature range 210- |                       |   |

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20. Abstract (continued)

295°K and the vapor pressure are calculated throughout the collapse of a supersaturated metastable vapor.

An effective molecular pair interaction energy and nearest neighbor coordination number is found based on the classical zero-point enthalpy of sublimation and by iteration to satisfy initial equilibrium limiting constraints at 273°K. The internal energy redistribution frequency results from close matching of the experimental pressure distribution. A method of determining the cluster size at which macroscopic properties become relevant is described; the size is found to be a cluster of about 122 molecules at 273°K based on a hard sphere model collision cross section. For the water vapor dimer an equilibrium constant of  $4.0 \times 10^{-21} (\text{cm}^{-3})$  is found at 273°K compared to  $3.1 \times 10^{-21} (\text{cm}^{-3})$  obtained from Keyes<sup>(3)</sup> data. Two models for water vapor clusters result (from satisfying all constraints imposed on the theory) which are given in terms of number of nearest neighbors, pair interaction energy per molecule ( $2.9 \text{ kcal/mol}$  at 273°K) and possible structure on a cluster by cluster basis for a classical hard sphere model and for a model approximating a Pauling type clathrate.  $\leftarrow$

$4 \times 10^{10}$  to  $10^{11}$  - 2.5 -  $\gamma$  units/cc

$3.1 \times 10^{10}$  to  $10^{11}$  - 2.5 -  $\gamma$  units/cc

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## I. ABSTRACT

The kinetic theory of cluster formation in a condensing gas proposed by Buckle<sup>(1)</sup> attempts to calculate the course of homogeneous condensation from molecular rather than thermodynamic precepts. Here it is applied to the rapid non-equilibrium expansion of atmospheric water vapor in air. A method is established for demonstrating the validity of this theory, originally proposed for a mono-molecular gas, in the case of a complicated species such as water vapor. Cluster conditions in the temperature range 210-295°K and the vapor pressure are calculated throughout the collapse of a super-saturated metastable vapor.

An effective molecular pair interaction energy and nearest neighbor coordination number is found based on the classical zero-point enthalpy of sublimation and by iteration to satisfy initial equilibrium limiting constraints at 273°K. The internal energy redistribution frequency results from close matching of the experimental pressure distribution. A method of determining the cluster size at which macroscopic properties become relevant is described; the size is found to be a cluster of about 122 molecules at 273°K based on a hard sphere model collision cross section. For the water vapor dimer an equilibrium constant of  $4.0 \times 10^{-21} \text{ (cm}^{-3}\text{)}$  is found at 273°K compared to  $3.1 \times 10^{-21} \text{ (cm}^{-3}\text{)}$  obtained<sup>(2)</sup> from Keyes<sup>(3)</sup> data.

Two models for water vapor clusters result (from satisfying all constraints imposed on the theory) which



are given in terms of number of nearest neighbors, pair interaction energy per molecule ( $2.9\text{kcal/mol}$  at  $273^\circ\text{K}$ ) and possible structure on a cluster by cluster basis for a classical hard sphere model and for a model approximating a Pauling type clathrate.

## II. FOREWARD

The work described here is an attempt at developing a method of applying the kinetic theory of cluster formation of E. R. Buckle<sup>(1)</sup> to experiments in supersonic nozzles. The patient support of the Power Branch and the Atmospheric Sciences Program, Office of Naval Research over many years and the recent support of the Naval Air Systems Command is acknowledged with many thanks. This effort has necessarily been an iterative one between theoretical development and numerical evaluation over more than ten years of investigation. Mathematical approximations were avoided from the start by relying on the digital computer from the start of development. Time-shared computer facilities were provided by the Naval Weapons Lab, Dahlgren, Virginia, as early as 1965 and since 1967 by the Naval Academy. The importance of interactive time-shared facilities which allow the investigator to treat the computer directly as a laboratory simulator is not to be underestimated, for without easy access to such a system this work could not have been completed.

The cluster theory<sup>(1)</sup> was developed for a binary mixture of monatomic gases and it seems a bit presumptuous to apply it to as complicated a system as water vapor in air. However, the best data and most clearly understood nozzle behavior was for such a mixture and at least a useful first approximation was hoped for. Moreover, the phenomenon of condensation is

universal and it was hoped that the solution could be worked out in terms of some such general manner, largely independent of the exact form of inter-molecular potentials. The end result is far better than expected and it appears that an average pair interaction energy can be used to describe as complicated a non-equilibrium interaction as that bonding a water molecule in a cluster.

The objective of this study is the development of a technique of applying the cluster theory<sup>(1)</sup> to the condensation of atmospheric water vapor in air while expanding in a supersonic nozzle (wind tunnel). Overall behavior of such flows is well understood<sup>7,8,9</sup> now and accurate measurement of experimental properties provides a means of comparison with theoretical results. It is attempted here to describe the course of the homogeneous condensation in a nozzle from molecular rather than thermodynamic parameters. Parametric studies of the influence of the adopted molecular parameters are given demonstrating the sensitivity of their influence on thermodynamic properties.

The general scheme is to establish a valid equilibrium initial value for the calculations, then by calculation follow the course of the expansion in a nozzle through the region of condensation<sup>7,8,9</sup>. Two models of water clusters evolve, one a hard sphere collision model and the other a clathrate type model more akin to water vapor. After establishing what

appears to be a valid initial equilibrium condition, the non-equilibrium expansion follows with a close matching of the experimental pressure to that calculated from the theory. One finds that the non-equilibrium cluster behavior is dominated by the behavior of the internal energy redistribution frequency.

The calculations described here were performed on a H-635 computer using the Dartmouth Time-Shared System (DTSS) with the long non-equilibrium calculations being performed on a Digital Equipment Corporation PDP-15/40 medium scale computer. The equilibrium solution requires about one minute while the non-equilibrium solution requires in excess of one hour.

The discussions over many years with Dr. W. Dunning, University of Bristol and with Dr. P. P. Wegener, Dr. B. T. Chu and other Yale University Researchers working on condensation, as well as Dr.'s B. N. Hale and P. L. M. Plummer at the University of Missouri-Rolla, were helpful and are acknowledged.

This work could not have been completed without the continuing advise and encouragement of E. R. Buckle, Sheffield University whose help was sincerely appreciated.

The author gives thanks to the Power above for allowing a glimpse into his very nature as seen in the dynamic beauty of these calculations.

### III. CLUSTER DISTRIBUTIONS AT EQUILIBRIUM

#### 1. Limiting Constraints

The cluster theory<sup>(1)</sup> is formulated such that non-stationary growth and decay rates of clusters of every size follow from phase integral specification of unimolecular and bimolecular reaction probabilities. Conceptually, each cluster was originally proposed as an assembly of atoms bound together by isotropic London forces. Consequently in extending this monomolecular theory to the polyatomic water molecule, one must accept an average value of the pair interaction energy complementing the isotropic London forces. As will be seen later this does yield meaningful results, even in the highly dynamic non-equilibrium situation considered later.

Furthermore, each molecule in a cluster can act as an oscillator with the number of vibrational degrees of freedom per cluster  $\chi_g$  determined by

$$\chi_g = 3g - 5, \text{ for the dimer;}$$

$$\chi_g = 3g - 6, \text{ for all larger sizes;}$$

$g$ , being the number of molecules in a cluster. The vibrational energy of these oscillators circulates within a cluster at frequency  $\bar{\nu}$ . As in any assembly of loosely coupled oscillators (with nearly similar vibrational characteristics), at any time a single oscillator may possess no energy or alternatively all of the energy. Before the latter condition could be realized, however, the unimolecular decay criterion<sup>(1)</sup> would cause the loss of that particular oscillator. That is, when

the energy of a single surface oscillator exceeds the "coupling" energy to its nearest neighbors it is lost from the cluster; this energy amounts to  $\lambda_g u_{11}^{\circ}$  where  $\lambda_g$  is the nearest neighbor coordination number and  $u_{11}^{\circ}$  is the pair interaction energy.

This decay energy or energy increment per loss (or gain) should not be confused with the cluster potential energy as in addition to the vibrational energy circulating from oscillator to oscillator, the cluster possesses energy binding it together; this is discussed further in III-8 and V-2.

Another parameter to be specified is  $\{\alpha_g\}^*$  which apportions some fraction of the  $\chi_g$  overall vibrational modes to be those of surface sites eligible for decay. The limiting constraints selected to obtain this parameter as well as those above are now considered.

The cluster theory independent parameters to be specified or determined are:

- $u_{11}^{\circ}$  - pair interaction energy
- $\bar{\nu}$  - cluster internal energy circulation frequency
- $\{\alpha_g\}_{g>1}$  - surface site to internal site parameter
- $\{\lambda_g\}_{g>1}$  - nearest neighbor coordination numbers
- $C_1$  - monomer concentration
- $g_{\infty}$  - cluster size of effective numerical infinity

\*{ } These brackets denote the set over all g.

where  $C_g$  is the stationary concentration ( $f_g$  is used for non-stationary states). It is the determination of these quantities from the limiting constraints that makes the solution unique to water. (In addition the collision cross sections, molecular masses involved, and some knowledge of the structure is required, see III-8). This is in marked contrast to a nucleation theory developed for a specific vapor<sup>(3)</sup> (water) where the vibrational characteristics of the particular molecule involved are included as parameters *within the theory*.

The limiting constraints to be satisfied here for saturated vapor equilibrium at any temperature far removed from the critical point are:

- (1) Equilibrium constant;  $\omega_\infty = \lim_{g \rightarrow g^\infty} \omega_g$
- (2) Zero temperature sublimation enthalpy;  $\Lambda_0 = \lambda_\infty u^\circ_{11}$
- (3) Saturated vapor pressure;  $p_v = \sum_{g>0} C_g kT$
- (4) Molecular number balance;  $C_{10} = \sum_{g>0} g C_g$
- (5) Incremental surface free energy change;  $\Delta\zeta = 0$   
 $g \rightarrow g^\infty$
- (6) \*Static pressure profile;  $\{p_k\} = \{p_k\}$   
theor. exp.

(calculated by starting from initial stationary  $\{C_g\}$ )

The computational procedure described next is iterative in nature; iterative within the equilibrium solution as well as between resulting equilibrium and non-equilibrium solutions.

\*Non-equilibrium condition satisfied later.

As will be seen later in V-2, even if satisfactory molecular descriptions of either the latent heat or surface tension were known, they would not be used instead of limiting constraint (6) to yield a complete evaluation of the theory because of the nature of  $\bar{v}$ . Approximate means of calculating these two parameters are proposed here but they are not used as limiting constraints.

The first of the variables discussed is  $\alpha_g$ , the surface site to internal site parameter. Recall from the cluster theory<sup>(1)</sup> that this parameter apports the fraction of total vibrational degrees of freedom that are decay vibrations, i.e., associated with surface sites. In the absence of a theoretical interpretation of this parameter in terms of the equations of molecular motion within the cluster, one must choose a model for the cluster structure. The very nature of the unimolecular decay mechanism in the theory obscures the precise effect of the internal structure of clusters, thus detail of this nature must come from other considerations.

The first approach is to envision a water vapor cluster as an assembly of hard spheres with collision cross sections defined in the classical sense<sup>(1)</sup>. For small size clusters all molecules would appear to be on the surface (See Figure VI-3.1) and paralleling the Pauling type clathrate cage where the first cage closes at size  $g = 20$  we define

$$\alpha = 1, \quad 2 \leq g < 20 \quad \text{III-1.1}$$



The cluster theory<sup>(1)</sup> yields a limiting value of  $\alpha_\infty$  for clusters having macroscopic properties in the equation preceding 8.14<sup>(1)</sup>, i.e.

$$\alpha_\infty = \lim_{g \rightarrow \infty} \alpha_g = \left(\frac{36\pi}{g}\right)^{1/3} \quad \text{III-1.2}$$

As will be seen later, the structure based on hard sphere collision diameters yields a value of  $g_\infty$  near 120. When  $g_\infty \approx 120$ ,  $\alpha_\infty \approx 0.98$  so the parameter  $\alpha_g$  remains near unity. The behavior imposed here for what might be called the hard sphere collision (HSC) is:

$$\begin{aligned} \alpha_g &= 1, & 2 \leq g \leq 20 \\ \alpha_g &= 1 - 0.1 \left(\frac{g}{g_\infty}\right), & g > 20 \end{aligned} \quad \text{III-1.3}$$

The variation of  $\alpha_g$ ,  $g > 20$  does not have a great overall effect on the cluster distribution. Calculations were performed with various forms of the expression for  $\alpha_g$  and gave only minor differences in the final result, the same cannot be said for the parameter  $\lambda_g$ , however (see below).

In the interest of closer approximating the structure of water clusters a second structure was considered (see following discussion on collision diameters and Section V-2). Implicit in this second model is the departure from Van der Waal type forces but with a structure and bonding more akin to water. Calculations with the model now designated as the water clathrate model (WCM) show a shift of  $g_\infty$  to about  $g = 200$  so  $\alpha_\infty$  becomes about 0.83. For this case we have

$$\alpha_g = 1 - 0.2 \left(\frac{g}{g_\infty}\right), \quad 20 < g < 200 \quad \text{III-1.4}$$

It will be seen that both models yield good results in predicting the dynamic behavior of non-stationary states (Section V-2).

For the hard sphere collision (HSC) corresponding to equation III-1.3, the hard sphere collision diameter is<sup>(1)</sup>

$$\sigma_{1,g} = r_1 (1+g^{1/3}) \quad \text{III-1.5}$$

A closer approximation to actual dimensions taken from a scale water clathrate model - WCM would be

$$\sigma_{1,g} = r_1 (1+2(g)^{1/3}), \quad \text{III-1.6}$$

which is used with  $\alpha_g$  described by equation III-1.4. The value of  $r_1$  used is  $1.4 \cdot 10^{-8}$  cm for all calculations. A summary on all aspects of both models is given in Section V-3.

## 2. Iteration Scheme

Having specified the independent parameters of the theory and the limiting constraints which must be satisfied, it is now shown how these conditions are met. Referring to the iteration scheme of Table III-2.1, one initiates the problem by selecting values of temperature  $T$ , pair interaction energy  $u_{11}^\circ$  and vibrational energy circulation frequency  $\bar{\nu}$ . A starting value of  $u_{11}^\circ$  was obtained by subtracting  $3kT$  (for rotation and translation modes and ignoring expansion work) from the latent heat *per molecule* at 273°K and equating the result to  $\lambda_\infty u_{11}^\circ$ . Selecting, arbitrarily,  $\lambda_\infty = 3.0$  gives a starting value of  $u_{11}^\circ = 2.98$  k cal/mole.

TABLE III-2.1

ITERATION SCHEME

|           |           |   |
|-----------|-----------|---|
|           | choose    | $T$ °K  |
|           | choose    | $u_{11}^{\circ}$ (limiting constraint 2)  |
| (A)       | choose    | $\bar{v}$   |
|           | calc.     | $C_1$ (perfect gas at saturation pressure<br>for $p \approx C_1 kT$ )   |
| (B)       | choose    | $C_1$ (since $p = \frac{\rho}{g} C_g kT$ )  |
|           | calc.     | $\lambda_{\infty}$  |
|           | calc.     | $F_{\theta}$ from $\omega_{\infty}$ , (a), (Limiting case $g \rightarrow g^{\infty}$ ,<br>$\omega(v, u_{11}^{\circ})$ )   |
|           | calc.     | $F(g, \theta)$ from $\omega_{\infty}$ , (b), ( $\omega_{\infty} = \text{MLF}(g, \theta) =$<br>$\omega(u_{11}^{\circ}, \lambda_{\infty})$ )  |
| (go to A) | ↑ compare | $F(\theta)$ & $F(g, \theta)$ if $F(a) \neq F(b)$ within $\epsilon$<br>modify $\bar{v}$ (limiting constraint 1)  |
|           | choose    | $g_{\infty}$ (Section III-3)  |
| (C)       | choose    | $m_{\lambda}$ (slope of $\lambda_g$ vs $g$ )  |
|           | calc.     | $\{C_g\}$   |
|           | calc.     | $P_v$   |
| (go to B) | ↑ calc.   | $C_{10}$ , if $p_v \neq p_v^{(4)}$ and $C_{10} \neq C_{1 \text{ initial}}$ ,<br>modify $C_1$ (limiting constraints 3 & 4)   |
| (go to C) | ↑ plot    | $\zeta$ , if $\Delta \zeta \neq 0$ at $g = g_{\infty}$ , modify $m_{\lambda}$<br>(limiting constraint 5)  |
|           |           | Use $\{C_g\}$ as initial condition for non-<br>equilibrium nozzle calculation. Follow<br>expansion down to onset of condensation<br>at pressure $p_k$ , if $\{p_k\}_{\text{theor.}} \neq \{p_k\}_{\text{exper.}}$ ,<br>modify $\bar{v}$ (limiting constraint 6) |

Choice of the vibrational energy circulation frequency raises questions on its relation to that of vibration spectra of water observed experimentally. For water vapor<sup>(4)</sup> there are frequencies associated with shifts in mean molecular position as well as with individual molecular vibrational modes; the former range from about  $10^{11}$  to  $10^{12}$   $\text{sec}^{-1}$  while the latter range upwards from  $10^{12}$   $\text{sec}^{-1}$  to well above  $10^{13}$   $\text{sec}^{-1}$ .

The cluster theory<sup>(1)</sup> assumes random distribution of the vibrational energy  $\chi_g kT$  circulating at frequency  $\bar{\nu}$  over  $\chi_g$  vibrational modes. In the classical approximation

$$\bar{\nu} \ll kT/h \quad \text{III-2.1}$$

(where  $h$  is Planks constant) such that the circulation frequency cannot exceed the frequency of any one vibration. It is assumed that the vibrational energy circulation frequency here is more closely related to water spectral frequencies associated with intermolecular vibrations (shifts in molecular position); this assumption is supported by later results (Section V-2). At the initial temperature of interest, 273°K, equality in equation III-2.1 gives

$$\bar{\nu} = 5.7 \times 10^{12} \text{ sec}^{-1}.$$

Next, the approximate manomer concentration  $C_1$  is calculated from the perfect gas law ( $p = CkT$ ) first taking  $C \approx C_1$  and a linear least squares fit of vapor pressure data for the liquid state<sup>(5)</sup>. It is assumed then that

$$p \equiv \sum_{g>0} C_g kT, \quad \text{III-2.2}$$

such that all clusters behave as a gas. The value of  $C_1$  calculated above from the perfect gas law must be reduced to account for the partial pressure of the clusters and at the same time maintain conservation of mass by molecular number balance in limiting constraint (4); this latter condition requires that the number of molecules of water in any distribution does not exceed the number calculated originally from the vapor pressure and the ideal gas law.

Once the initial value of  $u_{11}^{\circ}$  is chosen at the start of this iteration process, the value of  $\lambda_{\infty}$  is fixed by limiting constraint (2). The next step follows from the theory<sup>(1)</sup> as the equilibrium constant at saturation for the limiting case ( $g \rightarrow g^{\infty}$ ) is  $\omega_{\infty} = 1/C_1$ . This result comes from the definition of the parameter  $J$ ,

$$J \equiv \ln C_1/\omega_{\infty}, \quad \text{III-2.3}$$

which differs slightly from  $\ln$  of the saturation ratio because equation III-2.2. At saturation  $J = 0$  and  $C_1 = 1/\omega_{\infty} = C_{1s}$  so an alternate expression for  $J$  is

$$J = \ln C_1/C_{1s}. \quad \text{III-2.4}$$

Perhaps the most indirect of all the limiting constraints specified is condition (1) but this gives a means of selecting a value for the internal energy circulation frequency  $\bar{\nu}$  that satisfies other conditions of the theory. Consider first the equilibrium constant which results from detailed balance for

each  $g$  size (see {8}, reference 1 for complete details)

$$\omega \equiv C_g/C_1 C_{g-1} = ML_g F(g, \theta), \quad \text{III-2.5}$$

where  $M$ ,  $F$ ,  $G$  are convenient groupings defined by

$$M = (8\pi u_{11}^0/m_1)^{1/2} r_1^2/\bar{v}, \quad \text{III-2.6}$$

$$L(g>3, \theta) = (K_{g-1}/\alpha_g) \left( \frac{\chi_{g-1}}{n_{g-1}} \right) \left/ \left( \frac{\chi_{g-1}}{n_{g-1}} \right) \right., \quad \text{III-2.7}$$

$$K \equiv (\sigma_{1,g}/r_1)^2 / (\mu_{1,g}/m_1)^{1/2} \quad \text{III-2.8}$$

$$F(g, \theta) = (e^\theta/\theta^{1/2}) G(g, \theta), \quad \text{III-2.9}$$

$$G(g>3, \theta) = \{ \exp[\theta(\lambda_{g-1})] - \exp[\theta/(\lambda_g - \lambda_{g-1})] \} \\ / (1 + \lambda_g \theta + \lambda_g^2 \theta^2/2), \quad \text{III-2.10}$$

where  $\theta = u_{11}^0/kT$ ,  $m_1$  is molecular mass of water,  $\mu$  is the reduced mass and  $\lambda$  is the nearest neighbor coordination number.

In the thermodynamic limit of size <sup>(1)</sup> ( $g \rightarrow \infty$ ),  $K_{g-1} = g^{2/3}$ ,  $\alpha_g = (36\pi/g)^{1/3}$  and  $\lambda_g = \lambda_\infty$  giving the asymptotic values independent of size  $g$ .

$$L_\infty = (1/36\pi)^{1/3}, \quad \text{III-2.11}$$

$$F(g, \theta) = F(\theta) = [\exp(\lambda_\infty \theta) - 1/ \\ \theta^{1/2} (1 + \lambda_\infty \theta + \lambda_\infty^2 \theta^2/2)], \quad \text{III-2.12}$$

$$\omega_\infty = ML_\infty F\theta \quad \text{III-2.13}$$

Now, making use of the thermodynamic limit of size ( $g \rightarrow \infty$ ) at the condition of a saturated vapor ( $J=0$ ) gives, by equation III-2.3, III-2.11 and III-2.13

$$F(\theta) = \omega_\infty / ML_\infty = \frac{1}{C_{1s} ML_\infty} \quad \text{III-2.14}$$

allowing equality here with equation III-2.12. Having already defined values of  $u_{11}^{\circ}$  and  $\lambda_{\infty}$  in this iteration sequence some value of  $\bar{v}$  will satisfy both III-2.12 and III-2.14.

At this point some implicit conditions of the theory<sup>(1)</sup> must be satisfied. The surface free energy in terms of the equilibrium constants is

$$\zeta = -kT \sum_{i=2}^g \ln(\omega_i/\omega_{\infty}). \quad \text{III-2.15}$$

As  $\omega$  tends to  $\omega_{\infty}$  ( $g \rightarrow \infty$ ) and the clusters take on bulk properties (at saturated equilibrium), by equation III-2.15 the increment of surface free energy  $\Delta\zeta = \zeta_g - \zeta_{g-1}$  must approach zero; this requirement becomes limiting constraint (5). Also, by equation III-2.5 the value of  $\Delta\zeta$  is positive when  $G(\theta)/G(g,\theta) > L_g/L_{\infty}$ .

This important condition begins to limit the range of  $u_{11}^{\circ}$  and  $\bar{v}$ . In general, high values of  $u_{11}^{\circ}$  require high values of  $\bar{v}$  in order that  $\Delta\zeta$  be positive over all  $g$ ; too low a value of  $\bar{v}$  causes a hump in the distribution  $\{C_g\}$  with  $\Delta\zeta < 0$ . At the upper bound on  $\bar{v} = 5.7 \cdot 10^{12} \text{ sec}^{-1}$ ,  $u_{11}^{\circ}$  must be reduced to about 2.9 kcal/mole to satisfy the condition  $\Delta\zeta > 0$ ,  $g \rightarrow \infty$  as well as equations III-2.12 and III-2.14.

### 3. Numerical Infinity

In any numerical iteration technique an upper bound on the calculations must be specified. Selecting the value of cluster size corresponding to numerical infinity is considered next although this in reality is a separate iteration and an independent method of determining the size at which clusters

take on bulk properties. A first approximation at the value  $g_{\infty}$  is arrived at by the method described next, further refinement is a result of iteration to satisfy limiting constraint (5).

We must borrow from the following section the description used for surface coordination number for nearest neighbors,  $\lambda_g$ . The simplest behavior of this parameter would be a linear variation with cluster size. The slope of such a variation is taken as  $m_{\lambda}$ , which is, in fact, the incremental change in surface coordination number per unit increase of cluster size (above the trimer). The equilibrium computer program (See VIII-2) is now run with all variables held constant except for  $m_{\lambda}$ . An arbitrary value of this parameter yields a minimum (artificial) in a plot of the resulting saturated equilibrium cluster concentration versus size  $g$ . Defining the cluster size at the minimum in concentration as  $g=g^*$  and plotting this against the assumed value of  $m_{\lambda}$  gives the result in Figure III-3.1. The difference in the quantity  $\lambda_{\infty}-\lambda_{g^*}$  is also plotted;  $\lambda_{g^*}$  being the value of  $\lambda_g$  corresponding to the minimum in  $\{C_g\}$ .

As the value of slope  $m_{\lambda}$  is decreased the cluster size  $g^*$  at the minimum in  $\{C_g\}$  tends upward in size, the difference  $\lambda_{\infty}-\lambda_{g^*}$  approaches zero and as is shown next the increment in  $\Delta\zeta$  approaches zero. Below a slope of  $m_{\lambda} \approx 0.01$ , the minimum in  $g^*$  rapidly exceeds  $10^3$  (HSC). Once this approximate value of  $m_{\lambda}$  is determined it is further refined by iteration to satisfy limiting constraint (5).



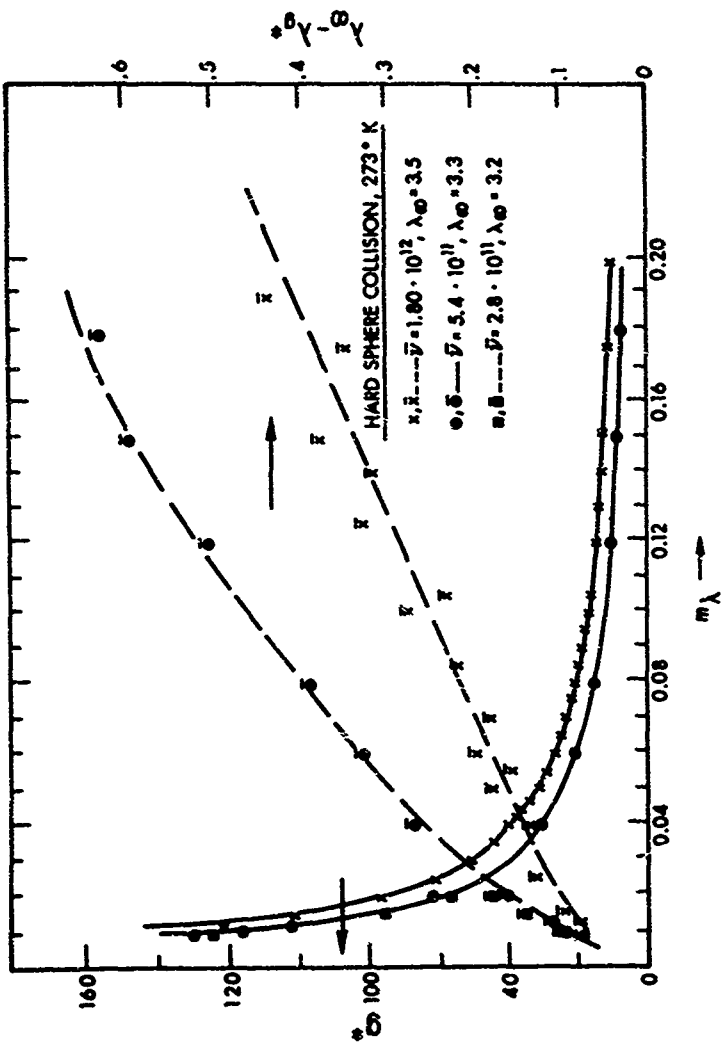


Figure III-3.1  
Approximate Numerical Infinity

In Figure III-3.1 the effect of determining  $g^*$  at several values of circulation frequency  $\bar{\nu}$  and  $\lambda_\infty$  is evident with no great change occurring with small variations in either parameter. The effect of slight changes of slope  $m_\lambda$  on surface free energy are shown in Figure III-3.2 indicating its sensitivity to structural variation. At a cluster size of about  $g=123$ ,  $\Delta\zeta$  is effectively zero (to three figure accuracy) for the hard sphere collision for the conditions shown.

#### 4. Nearest Neighbor Coordination Number

With regard to the variation of nearest neighbor coordination number  $\lambda_g$ , only the behavior with linear variation is present here; numerous other descriptions were attempted but satisfaction of the limiting constraints was not achieved. Considering the previous discussion on  $\alpha_g$  we see that no matter what model is considered (HSC or WCM) the first 20 molecules are prescribed as surface molecules; the immediate consequence is that  $\lambda_g$  is a surface coordination number for  $g \leq 20$ . Since we use equation III-1.3 to describe  $\alpha_g$  (HSC),  $g > 20$  nearly all of the other sites are surface sites and  $\lambda_g$  must be essentially a surface coordination number throughout. It will be seen later (V-2), that the principal contribution to the reaction dynamics is from small cluster sizes ( $g < 10$ ) so the distinction between surface and bulk coordination is unimportant for either the HSC or WCM case. In the absence of any further theoretical relation between  $\lambda_g$  and  $\alpha_g$  we assume the following. The upper limit of the set  $\{\lambda_g\}$  is  $\lambda_\infty$ .

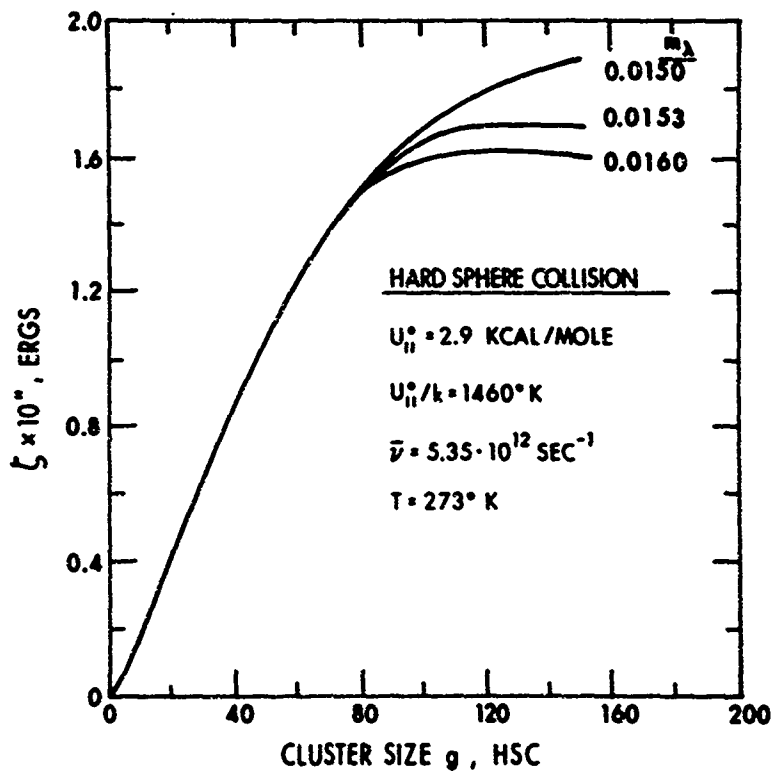


Figure III-3.2  
 Surface Free Energy

whose value is known from the asymptotic approximation discussed earlier (equation III-2.11 & III-2.13). A lower bound is also known since for the dimer,  $\lambda_2 = 1$  and for the trimer  $\lambda_3 = 2$ . Thus for  $g > 3$   $\lambda_g$  can vary only between the limits 2 and  $\lambda_\infty$ . For water (or ice) it is reasonable to suppose  $\lambda_\infty$  cannot be far removed from a value of 4.0 representative of tetrahedral coordination<sup>(4)</sup>.

Of the many variations of  $\lambda_g$  considered the following two linear models were most successful in satisfying the constraint:

$$\lambda_g = \lambda_3 + m_\lambda (g-3); \quad m_\lambda = \text{const.}, 3 < g < g_\infty,$$

$$\lambda_g = \lambda_\infty; \quad g > g_\infty, \quad \text{III-4.1}$$

and

$$\lambda_g = \lambda_3 + \frac{g}{g_\infty} (\lambda_\infty - \lambda_3); \quad 3 < g < g_\infty$$

$$\lambda_g = \lambda_\infty; \quad g > g_\infty \quad \text{III-4.2}$$

The second linear case, equation III-4.2, yields results quite similar to those of equation III-4.1 except that fine adjustment in  $m_\lambda$  allows attaining the zero change in incremental surface free energy required by limiting constraint (5), (See Figures III-3.2, and III-4.1 to 3) while adjusting  $g_\infty$  in equation III-4.3 does not. The behavior adopted henceforth is according to equation III-4.1.

The final limiting constraint, (6), which requires agreement between theoretical and experimental supersonic nozzle static pressure distribution is satisfied in section V-2.

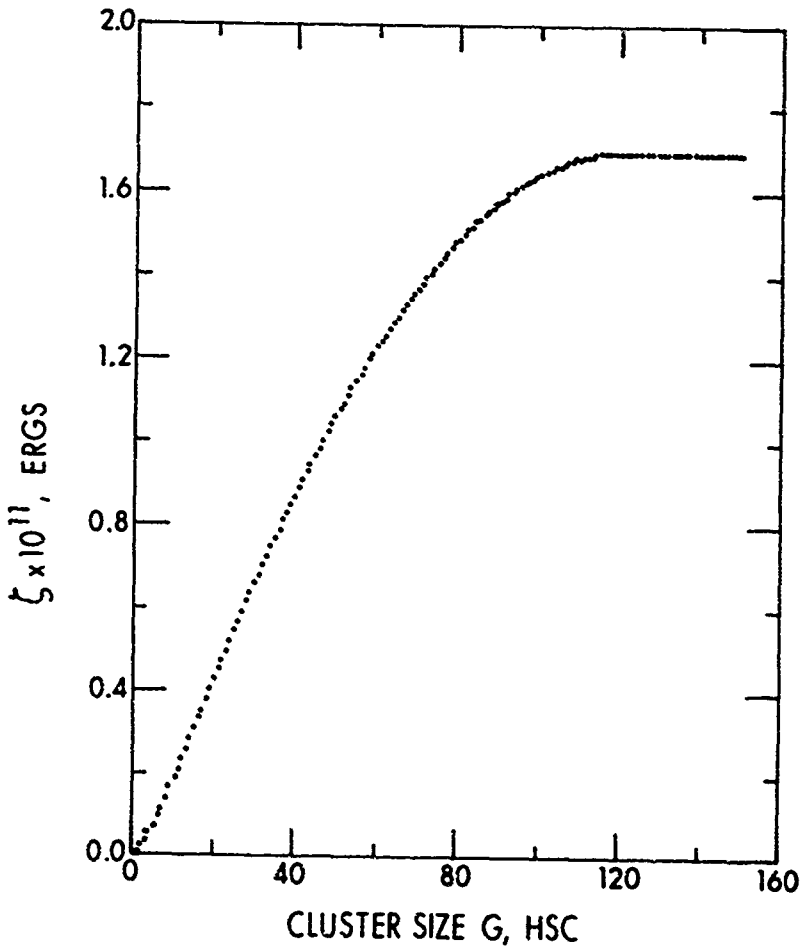


Figure III-4.1  
Surface Free Energy at Saturation, 273° K

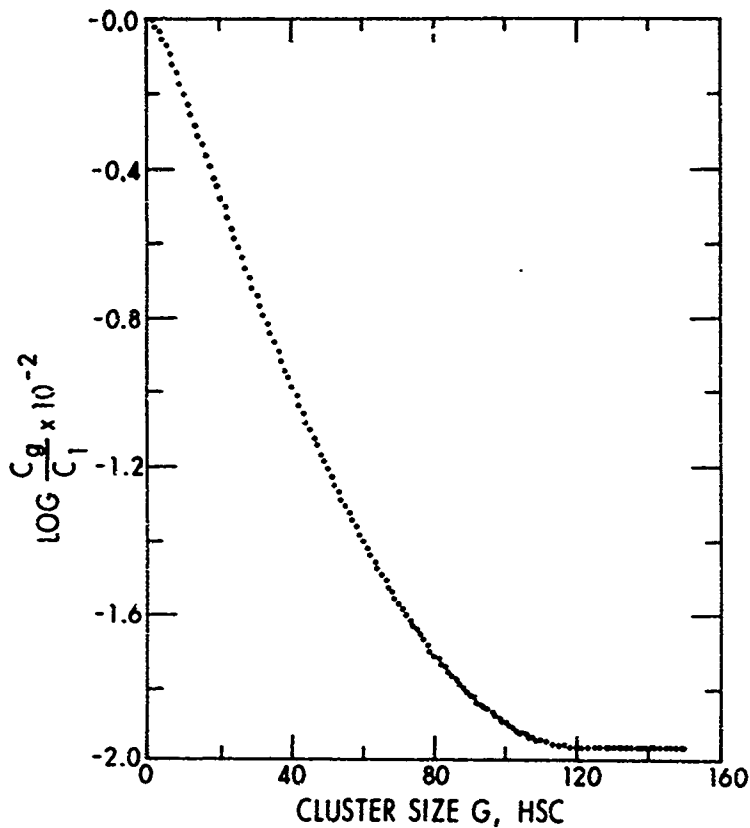


Figure III-4.2  
Concentrations at Saturation, 273° K

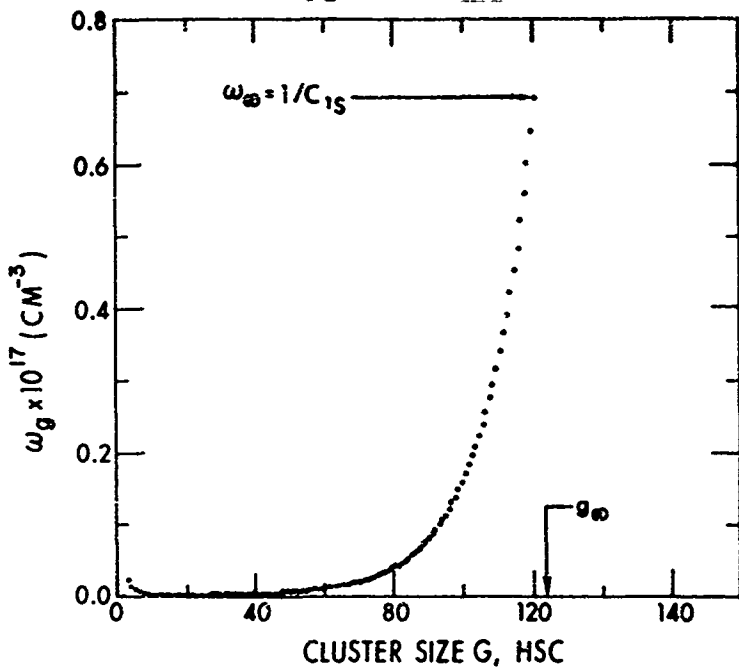


Figure III-4.3  
Equilibrium Constant, 273° K

Solution of the equations for saturated equilibrium (8.1 to 8.16, ref. 1) for the case of water vapor in air is given in a FORTRAN interactive computer program in Appendix 2 with the nomenclature given in Appendix 1. Corrections to reference 1 are given in Appendix 4. A summary of HSC results for several values of pair interaction energy is given in Table III-5.1. Results are also given for the dimer equilibrium constant for comparison with that obtained<sup>(2)</sup> from Keyes<sup>(6)</sup> data.



## 5. Results at Saturated Equilibrium

When one succeeds in satisfying limiting constraints (1) through (5), the results appear (HSC) as in Figures III-4.1 to III-4.3. At conditions of saturated equilibrium, satisfying boundary condition (5) also implies that  $\Delta C_g = 0$  as  $g \rightarrow g_\infty$ . This is evident from the equilibrium distribution<sup>(1)</sup>

$$C_g = C_1 \exp[(g-1)J - \zeta_g/kT], \quad \text{III-5.1}$$

which at saturation ( $J=0$ ) is

$$C_g = C_1 \exp[-\zeta_g/kT]. \quad \text{III-5.2}$$

i.e., at a given temperature the variation in  $\{C_g\}$  at saturation is entirely dependent on the incremental change in surface free energy  $\Delta \zeta_g$  with cluster size. The use of the concept of an effective numerical infinity is tantamount to the assumption that clusters of size  $g \approx g_\infty$  exhibit bulk properties.

In Figure III-3.2 it is evident that the distribution  $\{C_g\}$  is quite sensitive to the variation in  $\{\lambda_g\}$ . A zero value of the slope  $m_\lambda$  in equation III-4.1 yields a nearly linear decreasing distribution  $\{C_g\}$  with, of course, no minimum appearing. A finite value of  $m_\lambda$  causes a minimum in the distribution  $\{C_g\}$  with limiting constraint (5) requiring that this minimum occur at effective numerical infinity. In the WCM case, Figure III-5.1 shows that the minimum in  $\{C_g\}$  or alternatively  $\Delta \zeta \rightarrow 0$  has shifted outward to the neighborhood of  $g_\infty \approx 200$ .

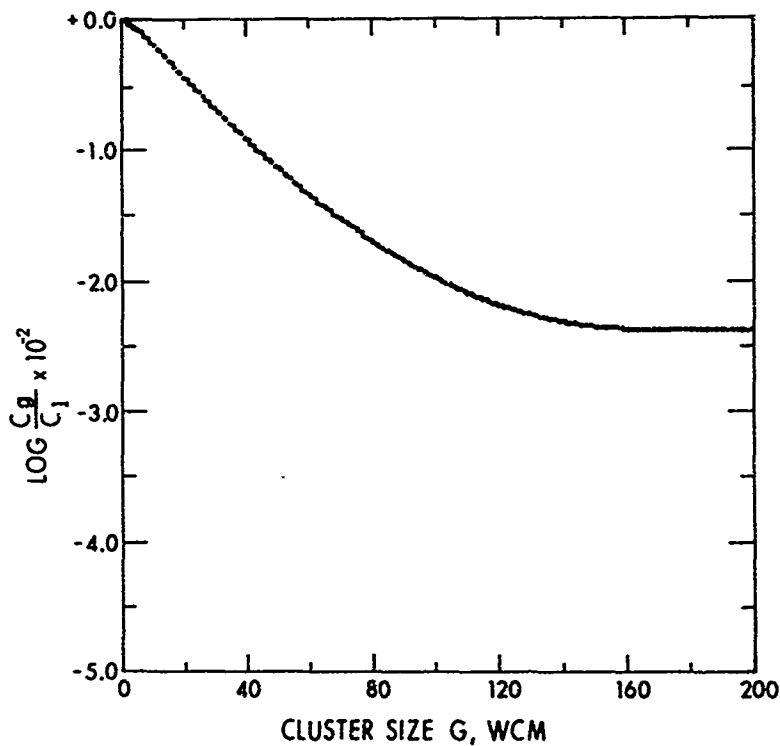


Figure III-5.1  
Concentrations at Saturation, 273° K

TABLE III-5.1

## EQUILIBRIUM RESULTS AT 273°K

## 1) HARD SPHERE COLLISION (HSC)

| Case | $u_{11}^0/k(^{\circ}K)$ | $u_{11}^{\circ}$ (Kcal/mole) | $\bar{v}$ (sec $^{-1}$ ) | $C_1$ (cm $^{-3}$ )  | $\lambda_{\infty}$ | $g_{\infty}$ | $m_{\lambda}$ | $p_v$ (cmHg) | $C_{10}$ (cm $^{-3}$ ) | $\omega_2$ (cm $^{-3}$ ) |
|------|-------------------------|------------------------------|--------------------------|----------------------|--------------------|--------------|---------------|--------------|------------------------|--------------------------|
| a    | 1387*                   | 2.76                         | $5.30 \cdot 10^{12}$     | $1.60 \cdot 10^{17}$ | 4.10               | 124          | 0.0169        | 0.452        | $1.60 \cdot 10^{17}$   | $3.11 \cdot 10^{-21}$    |
| b    | 1421**                  | 2.82                         | $5.35 \cdot 10^{12}$     | $1.60 \cdot 10^{17}$ | 4.00               | 123          | 0.0162        | 0.452        | $1.60 \cdot 10^{17}$   | $3.50 \cdot 10^{-21}$    |
| c    | 1460                    | 2.90                         | $5.35 \cdot 10^{12}$     | $1.60 \cdot 10^{17}$ | 3.90               | 124          | 0.0153        | 0.452        | $1.60 \cdot 10^{17}$   | $4.02 \cdot 10^{-21}$    |
| d    | 1500                    | 2.98                         | $5.31 \cdot 10^{12}$     | $1.60 \cdot 10^{17}$ | 3.79               | 124          | 0.0144        | 0.452        | $1.60 \cdot 10^{17}$   | $4.69 \cdot 10^{-21}$    |

## 2) WATER CLATHRATE MODEL (WCM)

|   |      |      |                      |                      |      |     |        |       |                      |                       |
|---|------|------|----------------------|----------------------|------|-----|--------|-------|----------------------|-----------------------|
| c | 1460 | 2.90 | $5.35 \cdot 10^{12}$ | $1.60 \cdot 10^{17}$ | 3.90 | 195 | 0.0097 | 0.452 | $1.60 \cdot 10^{17}$ | $4.02 \cdot 10^{-21}$ |
|---|------|------|----------------------|----------------------|------|-----|--------|-------|----------------------|-----------------------|

\*Iteration to satisfy dimer equilibrium constant  $\omega_2 = 3.1 \cdot 10^{-21}$  obtained (2) from Keyes data (6)

\*\*Iteration to give  $\lambda_{\infty} = 4.0$

## 6. Variations with Temperature

The computer program of Appendix 2 gives results at saturated equilibrium at any temperature by varying the input temperature. Having satisfied boundary condition (1) through (5) at 273°K, the parameters listed in Table III-5.1(c) were used at the other temperatures given. The monomer concentration satisfying boundary conditions (3) and (4) was the only iteration performed with the end result that condition (3) was satisfied at the temperatures given. The HSC concentrations obtained are given in Figure III-6.1 with the net result that boundary condition (5) was satisfied over the range 290°K-230°k. (See later discussion on  $\bar{v}$ , however, in Section V-2 with regard to condition (1)).

## 7. Surface Tension of Clusters

Theory<sup>(1)</sup> gives for the small cluster property corresponding to the specific tension in the vapor-liquid interface

$$\Gamma = (\zeta_g/g\alpha) (\rho/m_1)^{2/3}, \quad \text{III-7.1}$$

which differs from the classical result obtained by equating the product of surface area and surface tension equal to surface free energy, i.e.:

$$\Gamma = (\zeta_g/g^{2/3}) (\rho/m_1)^{2/3} / (36\pi)^{1/3}, \quad \text{III-7.2}$$

where in effect  $\alpha = (36\pi/g)^{1/3}$ , but note that this is  $\alpha$  for a flat surface (cf. line 3, pg. 1280, Ref. 1). Early attempts at evaluating the theory included satisfying equation III-7.1 as a boundary condition. Examination of results in Figure

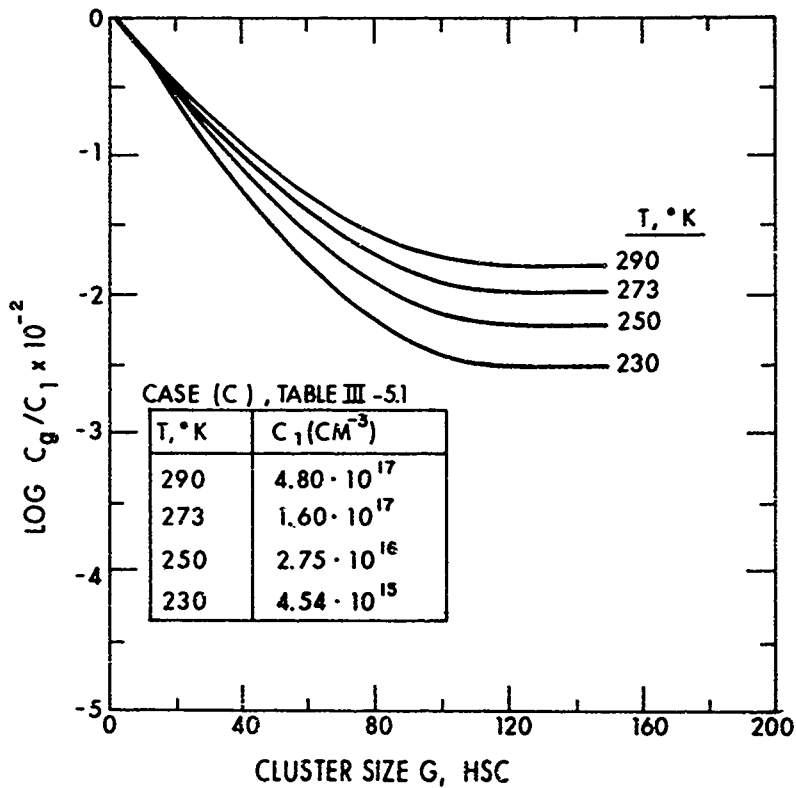


Figure III-6.1  
Concentrations at Saturation, 290° to 230° K

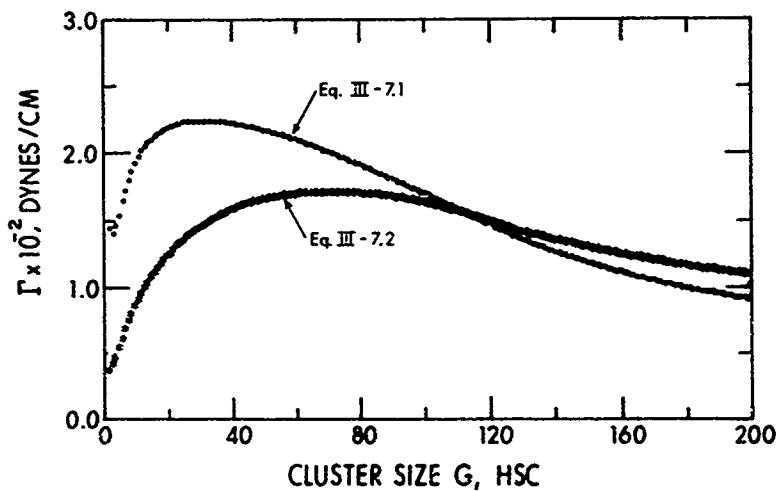


Figure III-7.1  
Surface Tension Variation, Saturation 273° K

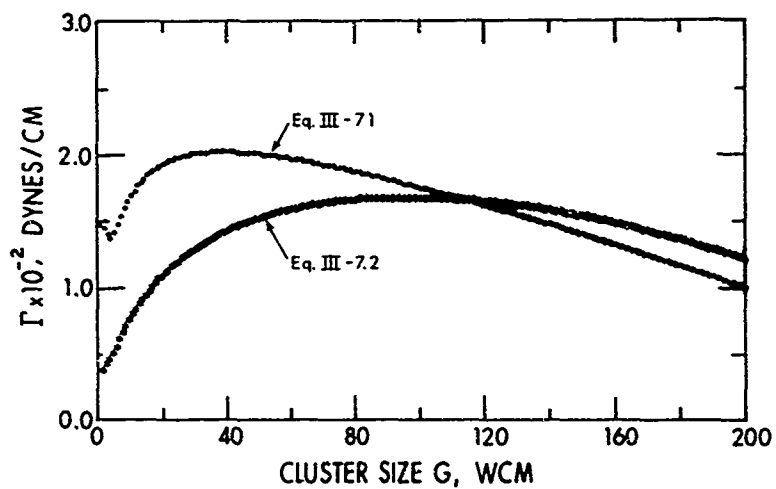


Figure III-7.2  
Surface Tension Variation, Saturation 273° K

III-7.1, however, shows that for the Hard Sphere Collision, macroscopic levels ( $\sim 75$  dynes/cm at 273°K) are not reached until the cluster size approaches  $g = 200$  using equation III-7.1, or much larger sizes by equation III-7.2. To conform with conditions specified thus far, for  $g < g_{\infty} \approx 124$  equation III-7.1 is appropriate and for larger size, equation III-7.2 would seem more appropriate. Results in Figure III-7.2 for WCM indicate that macroscopic levels of surface tension would not be attained in either case until sizes in excess of about 250 were reached.

The net result is that the use of surface tension as a limiting constraint precludes the possibility of satisfying all other limiting conditions imposed. It appears that the simple molecular viewpoint used to interpret the equilibrium theory here requires that the property  $\Gamma$  corresponding to small clusters be considered higher than the macroscopic, even at the cluster size satisfying other limiting constraint for  $g > g_{\infty}$ .

#### 8. Latent Heat

As a possible alternative limiting constraint the thermodynamic property known as latent heat was considered. In the absence of a molecular description of this property the following crude model is proposed.

Consider the energy added to a system in going from the liquid to vapor state (at constant pressure, temperature) as the energy used in breaking bonds in the liquid to establish



and energize an equilibrium population of monomer, dimer, trimer, etc. in the vapor plus the work in moving the system boundaries. In the liquid state some of the nearest neighbors may be hydrogen bonded in tetrahedral coordination<sup>(4)</sup>, others may not be involved in hydrogen bonds. The fraction not involved in such bonding may be as high as about 0.6 at 273°K with most results<sup>(4)</sup> predicting a value near 0.5. A crude attempt is made below to allow for the overall effect of such unbonded water molecules in the liquid state.

In proposing this crude model of latent heat some knowledge of the structure of water clusters is required. Cluster structure which evolved in the course of the iterations to satisfy limiting condition (6) is discussed in section V-4 and the resulting number of bonds  $\eta_g$  per cluster is given in Table III-8.1 for both the HSC and WCM. The bonding scheme is important because the energy stored in these bonds must be considered as cluster internal potential energy in addition to its vibrational energy.

TABLE III-8.1  
BONDING ARRANGEMENT

| <u>Liquid</u>                        | <u>Vapor</u> | <u><math>\eta</math>, HSC</u> | <u><math>\eta</math>, WCM</u> |
|--------------------------------------|--------------|-------------------------------|-------------------------------|
| $\eta = \lambda_\infty = 4$ , bonded | monomer      | 0                             | 0                             |
|                                      | dimer        | 1                             | 1                             |
| $\eta < 4$ , unbonded                | trimer       | 2                             | 2                             |
|                                      | g-mer        | $g\lambda_g/2$                | $g-1$                         |

For hydrogen bonded molecules in the liquid state with tetrahedral coordination, removal of a single molecule is taken here as the breaking of  $\lambda_{\infty} = 4$  bonds; in the non-hydrogen bonded case the number is lower and is discussed below.

Using these concepts, for each dimer formed two molecules have their bonding changed from  $n = \lambda_{\infty}$  (liquid) to  $n_2$  (vapor). Assuming pairwise additive interactions for nearest neighbors (at absolute zero in temperature) the energy required to separate infinitely a single molecule from the liquid is  $\lambda_{\infty} u^{\circ}_{11}$ . In forming the dimer, two such actions are required and the energy regained on bringing two infinitely separated molecules to form a dimer is  $\eta_2 u^{\circ}_{11}$ . Hence, the energy required to produce a dimer from the liquid (at  $T=0$ ) is  $(2\lambda_{\infty} - \eta_2) u^{\circ}_{11}$ . By similar reasoning, we have a g-mer:  $(g\lambda_{\infty} - \eta_g) u^{\circ}_{11}$ . There does not appear to be any reliable method of predicting what fraction of the liquid state molecules are hydrogen bonded in tetrahedral coordination, so simple reduction of  $\lambda_{\infty}$  (liquid) from 4.0 to a lower value determined by iteration is introduced to give an overall or effective  $\lambda_{\infty}$  in the liquid state. Thus a resulting value of  $\lambda_{\infty} = 4.0$  would imply 100% bonding in tetra-hedral coordination; a lesser value implies the presence of unbonded molecules in the liquid state. Next, to adjust for temperature above zero we must add an amount of energy equal to the difference in thermal energies of the g molecules in the gaseous and liquid states as well as the work of moving the system boundary

outward from the liquid state to that encompassing both liquid and vapor. This additional volume is that required to allow full thermal energy for each cluster in the vapor.

We can now express the T=0 energy difference from liquid to vapor, say for the dimer as (in ergs per cc of dimer):

$$(g\lambda_{\infty} - \eta_g) u_{11}^{\circ} \frac{\text{bonds broken (net)}}{\text{dimer formed}} \times C_2 \frac{\text{dimers formed}}{\text{cm}^3} \times u_{11}^{\circ} \frac{\text{ergs}}{\text{bond}} \quad \text{III-8.1}$$

For any other size, including the monomer we have  $(g\lambda_{\infty} - \eta_g) C_g u_{11}^{\circ}$  or in establishing the entire equilibrium population:

$$L^{\circ} = \sum_{g>0} \frac{L^{\circ}}{g} = \sum_{g>0} (g\lambda_{\infty} - \eta_g) C_g u_{11}^{\circ} \quad \text{III-8.2}$$

where  $\eta_g = g\lambda_g/2$  HSC,  $g-1$  WCM.

In addition to this, energy added to a system to vaporize it must do work against its boundaries and increase the kinetic energy from that in the liquid state to that of the vapor; here the kinetic energy of the liquid state is neglected. As in the theory<sup>(1)</sup> the clusters have vibrational, rotational and translational energy with the rotational and translational degrees of freedom for the water taken as 6, the dimer as 5 and all others are taken as 6. The vibrational energy is described by<sup>(1)</sup>

$$\epsilon_v = \chi_g kT \quad \text{III-8.3}$$

where  $\chi_g = 3g-5$  for the dimer and  $3g-6$  for  $g>2$ . At constant pressure and temperature, the expansion work per molecule is

pv or considering the clusters as a perfect gas  $pv=kT$ .

Thus:

$$L' = L^\circ + \text{Energy}(\text{trans, rotat., vib.}) + \text{Work}$$

$$L' = L^\circ + \frac{6}{2} kT(C_1) + \frac{5}{2} kT(C_2) \\ + \frac{6}{2} hf \sum_{g=3}^{g_\infty} C_g + kT \sum_{g=2}^{g_\infty} \chi_g C_g \\ + kT \sum_{g>0} C_g. \quad \text{III-8.4}$$

To compare this result with accepted data in the literature, such as  $L = 595.5 \text{ cal/g}$  at  $273^\circ\text{K}$ <sup>(5)</sup>, the total mass  $\mu_T$  in grams for the population  $\{C_g\}$  is required. Here

$$\mu_T = m_1 V \sum_{g>0} g C_g \quad \text{III-8.5}$$

where  $m_1$  is the mass of a single molecule and  $V$  is the total volume occupied. Consequently the density is given by  $\mu_T/V \text{ g/cm}^3$ . Thus tabular values<sup>(5)</sup> of latent heat  $L$  are converted to  $\text{cal/cm}^3$  by

$$L' = (L \text{ cal/gram}) (m_1 \sum_{g>0} g C_g \text{ g/cm}^3). \quad \text{III-8.6}$$

Now, equating the results in equations III-8.4 and III-8.6 gives

$$L = \frac{u^\circ ll}{m_1} \sum_{g>0} \frac{(g\lambda_\infty - \eta_g) C_g}{\sum g C_g} + \frac{6}{2} \frac{kT}{m_1} \frac{C_1}{\sum_{g>0} g C_g} \\ + \frac{5}{2} \frac{kT}{m_1} \frac{C_2}{\sum_{g>0} g C_g} + \frac{6}{2} \frac{kT}{m_1} \frac{\sum_{g=3}^{g_\infty} C_g}{\sum_{g>0} g C_g} \\ + \frac{kT}{m_1} \frac{\sum_{g=2}^{g_\infty} \chi_g C_g}{\sum_{g>0} g C_g} + \frac{kT}{m_1} \frac{\sum_{g>0} C_g}{\sum_{g>0} g C_g} \quad \text{III-8.7}$$

which allows direct comparison with known values of latent heat in units of cal/g.

Iteration for  $\lambda_{\infty}$  (effective) in equation III-8.7 for the liquid state at 273°K yields a value of 3.04 with L = 595.7 cal/g (HSC) and the term by term contribution to  $\zeta$  is given in Table III-6.2.

TABLE III-6.2

| Results of equation III-8.7 at 273°K, L = 595.7 cal/g, HSC and WMC |      |      |        |       |      |      |
|--|------|------|--------|-------|------|------|
| Term   | 1    | 2    | 3      | 4     | 5    | 6    |
| Magnitude, cal/g   | 478  | 88.2 | 0.0047 | 0.002 | 0.02 | 29.4 |
| % contribution   | 80.2 | 14.8 | nil    | nil   | nil  | 4.9  |

with the monomer accounting for nearly all the energy. The solution of case (c) Table III-5.1 was employed here with identical results for both WCM and HSC because of the dominance of the monomer.

It does not appear fruitful to speculate further on the possible fraction of unbonded molecules in the liquid state. Reduction of  $\lambda_{\infty}$  from 4.0 to 3.04 with the nearest neighbor concept employed here does imply unbonded molecules in the liquid but the fraction is still unknown. The majority still could be in tetrahedral coordination with an appreciable fraction involved in fewer bonds.

Due to the uncertainties involved, the latent heat was not used as a limiting constraint in this work.

#### IV. CLUSTER DISTRIBUTIONS FOR SUPERSATURATED AND UNDERSATURATED CONDITIONS

##### 1. Experimental Realization

The system considered is that of a dilute solution of water vapor in a carrier gas of air. To examine the states traversed by this mixture while it expands adiabatically in a nozzle it is convenient to refer to Figure IV-1.1 in coordinates of  $\log p$  and  $\log T$ . For the adiabatic expansion of the mixture  $p = cp^{\gamma_i}$  where  $\gamma_i = c_p/c_v$  and is to a close approximation equal to the ratio of specific heats of air, and  $p = \rho R t$ . The slope of the adiabat (ABC) is only a function of the specific heat ratio ( $\gamma_i$ ) of the carrier gas

$$\frac{d(\log p)}{d(\log T)} = \frac{\gamma_i}{\gamma_i - 1} \quad \text{IV-1.1}$$

while for the vapor the saturation line (A'C') is obtained from data<sup>(5)</sup> or the Clausius-Clapeyron relation and  $p = \rho R t$ :

$$\log p_s = 9.3286 - 2367.713/T, \quad 300 < T < 250 \quad \text{IV-1.2}$$

The vapor and carrier gas temperature are assumed identical at all times<sup>(1)</sup>. For a mixture initially at point A, the vapor state is undersaturated and  $J < 0$ <sup>(1)</sup>. Adiabatic cooling of the mixture occurs on expansion, with saturation at point B. Beyond point (B) the vapor is supersaturated with apparent collapse of supersaturation beginning at, say, C. Cluster distributions corresponding to thermodynamic equilibrium from point A to C are now considered with those beyond examined later.

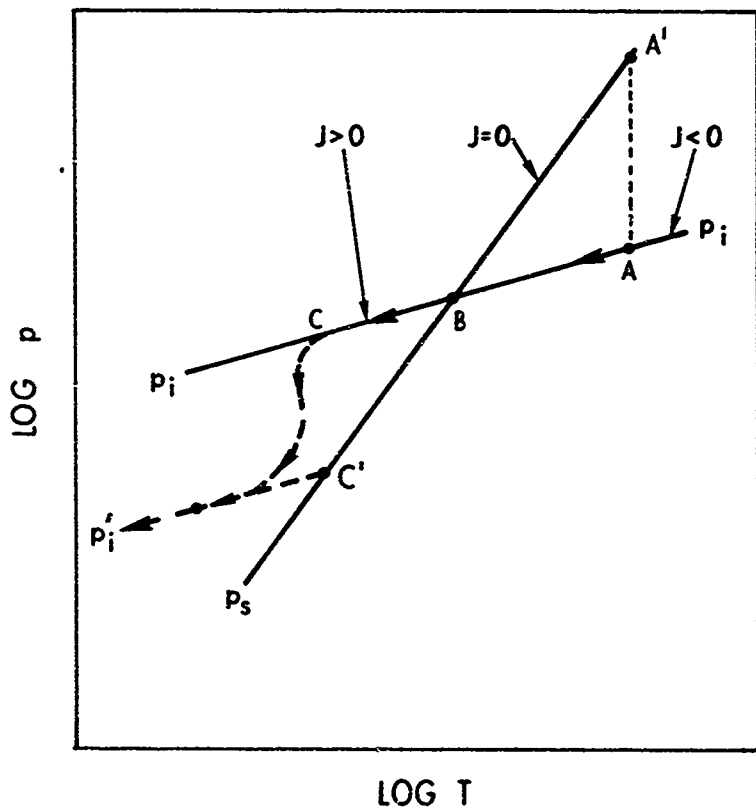


Figure IV-1.1  
 Hypothetical State Diagram for Adiabatic Expansion  
 of Water Vapor in Moist Air  
 A'B'C' Saturation Line; ABC Adiabatic Line

Point A is typical of the initial condition encountered in the experiments described later. The undersaturated condition at point (A) where  $J < 0$  follows from equation III-5.1. Since  $J = \ln C_1 / \omega_\infty = \ln C_1 / C_{1s}$ , the monomer concentration  $C_{1s}$  at saturation (A') (at the temperature of point (A) must be calculated to define  $J_A$ . Conditions at (A') are known from the solution of Appendix (a) with iterations satisfying the saturation pressure equation IV-1.2, other parameters are retained from the results at 273°K. Once  $C_{1s}$  is known, the calculation is rerun yielding the stable undersaturated ( $J < 0$ ) distribution (a), (296°K), given in Figure IV-1.2.

For the supersaturated condition ( $J > 0$ ) again as in the undersaturated case the equilibrium equations must first be solved for  $C_{1s}$ . Once  $C_{1s}$  is known the solution proceeds as before with limiting constraints (3) replaced by the iteration for the isentropic pressure

$$P_i = 0.452 \left( \frac{T}{273} \right)^{\frac{Y_i}{Y_i - 1}} \quad \text{IV-1.3}$$

Typical results for temperatures encountered in later experiments are given in Figure IV-1.2. As noted in the theory<sup>(1)</sup> the minimum present in  $\{C_g\}$  when  $J > 0$  corresponds to Volmer's critical size at  $g = g^*$ . For further discussion of this point see Section VII.



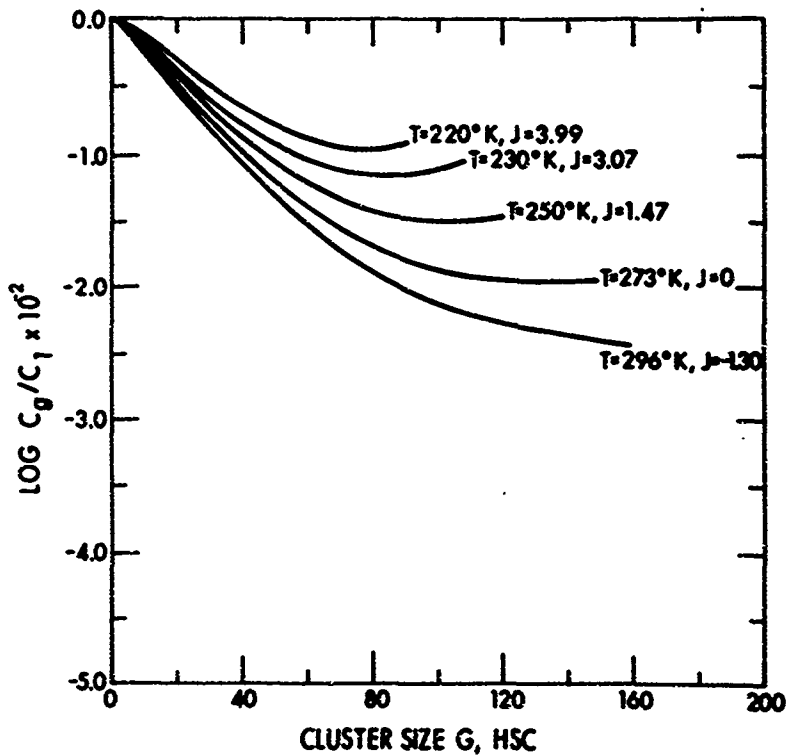


Figure IV-1.2  
Equilibrium Under Saturated, Saturated and  
Supersaturated Conditions

## V. NON-EQUILIBRIUM AND RELAXATION CONSIDERATIONS

### 1. Constant Volume Quenching

In order to begin to compare the results of numerical analysis with experimental data, initial equilibrium conditions for the calculation must be known. Once the basic predictions of the theory of equilibrium are in hand it is possible to employ these results as initial conditions and begin the calculations involving a gradual departure from equilibrium; such is the case in the rapid expansion of a condensable vapor in an inert carrier gas. However, inasmuch as an adiabatic expansion is difficult to interpret on the molecular scale, it is useful to examine first the constant volume quenching process and then to proceed to the case of a steady expansion.

Consider a mixture of saturated vapor with a cluster population  $\{C_g\}$  and inert gas initially in thermal equilibrium subjected to infinitely rapid cooling to a supersaturated state and maintained thereafter at constant volume. The clusters present initially at equilibrium are thus subjected to quenching with the rates of cluster growth exceeding the rates of cluster decay tending, in effect, towards condensation with an exothermal rate of heat production.

To calculate this heat production consider the gas phase reaction by collision of an  $A_{g-1}$  cluster and a  $A_1$  monomer to give an  $A_g$  cluster



in the interval during which the temperature  $T$  is constant and the total volume is unchanged. The kinetic theory of cluster formation <sup>(1)</sup> specifies the energy release associated with this reaction as  $\lambda_g u_{g-1}^0$ , the product of the nearest neighbor surface coordination number and the Van der Waals pair interaction energy. The objective here is to specify the net exothermal heat of reaction associated with all reactions, Eq. V-1.1 for a cluster population  $\{C_g\}_{g>1}$  subjected to a rapid quench (or heat bath).

Several approaches to this problem were considered over the years with the most promising result given here. To describe the energy of reaction of V-1.1 an energy balance is first taken on the bimolecular mechanism

$$A_{g-1} + A_1 = A_g$$

and then followed with the unimolecular process

$$A_g = A_{g-1} + A_1$$

within a fluid element of constant volume, temperature and concentration.

Consider first the bimolecular reaction

$$A_{g-1} + A_1 \rightarrow A_g$$

proceeding forward at rate  $R_g^+$ . For every  $A_g$  cluster formed at rate  $R_g^+$  from an  $A_{g-1}$  cluster, 1 monomer is 'consumed' and  $\lambda_g u_{g-1}^0$  energy of reaction is involved per  $A_{mer}$  formed. A general energy balance on the element is (where  $\dot{\epsilon} = dc/dt$ )

$$\dot{\epsilon}_{in} + \dot{\epsilon}_{liberated} = \dot{\epsilon}_{out} + \dot{\epsilon}_{stored}^0$$

with bimolecular input equal to

$$\dot{\epsilon}_{in,bi}^{lib} = \epsilon_{g-1}^0 R_g^+ + \epsilon_{g-1}^T R_g^+ + \epsilon_1^T R_g^+ + \epsilon_g^R R_g^+ \quad V-1.2$$

per cluster. The reaction rate expressions from the theory are summarized in Table V-1.1. Energy  $\epsilon^0$  is the zero point cluster energy equal to the sum of all pair interaction energies within a cluster at zero temperature. This energy can be viewed as cluster internal or potential energy involving all molecules, both bulk and surface, of each cluster. Energy  $\epsilon^T$  is the thermal energy corrections for temperatures above absolute zero contributed by the thermally-excited degrees of freedom previously defined (Section III-8). Thus, for the particles involved in this reaction we have:

| <u>Particle</u> | <u>Energy</u>  |       |
|-----------------|--|-------|
| $A_g$           | $\epsilon_g^T = \epsilon_g \text{ int.} + \epsilon_{g,rot.} + \epsilon_g \text{ transl} =$                       |       |
|                 | $x_g \text{ kT} + \frac{1}{2} \epsilon_g \text{ kT} + \frac{1}{2} S_g \text{ kT}$                                |       |
| $A_{g-1}$       | $\epsilon_{g-1}^T = x_{g-1} \text{ kT} + \frac{1}{2} \epsilon_{g-1} \text{ kT} + \frac{1}{2} S_{g-1} \text{ kT}$ |       |
| $A_1$           | $\epsilon_1^T = x_1 \text{ kT} + \frac{1}{2} \epsilon_1 \text{ kT} + \frac{1}{2} S_1 \text{ kT}$                 | V-1.3 |

Finally, we have  $\epsilon^R = \lambda_g u_{11}^0$  as the energy liberated in the bimolecular reaction (1). It is important to focus attention on the individual particles involved as it is the (g-1) size cluster and the monomer which enter the fluid element while the reaction "within" the element is written for the (g) size

TABLE V-1.1  
SUMMARY OF NON-EQUILIBRIUM RATE EQUATIONS

$$\frac{df_g}{dt} = R_g^+ - R_{g+1}^+ + R_{g+1}^- - R_g^-$$

where:  $\theta = u_{11}^0/kT$ , and  $\gamma^2 = u_{00}^0/u_{11}^0$ ;

$$R_2^+ = z_{0,1}'' f_0 \underline{f_1} z_{1,01}'' \underline{f_1} \gamma^\theta (1-e^{-\theta}) / v_{01}$$

$$R_2^- = z_{0,1}'' f_0 z_{1,01}'' f_2 \bar{v} \gamma \theta e^{-\theta} (1-e^{-\theta}) z_{1,1}'' v_{01}$$

$$R_3^+ = z_{1,2}'' \underline{f_1} f_2 (1-e^{-\theta})$$

$$R_3^- = \bar{v} f_3 e^{-2\theta} (1+2\theta) / 2$$

$$R_4^+ = 2z_{1,3}'' f_1 f_3 (1-e^{-\lambda_3 \theta}) / (\chi_3) (\chi_3 - 1)$$

$$R_{g>4}^+ = 6 z_{1,g-1}'' f_1 f_{g-1} (1-e^{-\lambda_{g-1} \theta}) / \chi_g (\chi_{g-1} - 1) (\chi_{g-1} - 2)$$

$$R_{g>3}^- = 2 \alpha_g \bar{v} f_g e^{-\lambda_g \theta} (1 + \lambda_g \theta + \frac{1}{2} \lambda_g^2 \theta^2) / (\chi_g - 1) (\chi_g - 2)$$

cluster. In essence we make an energy balance (bimolecular part of reaction) only on the new particles  $df_{g,bi} = R_g^+ dt$  entering the element as  $f_g$  remains constant with the element.

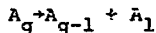
The energy out of the fluid element associated with the bimolecular reaction is

$$\dot{\epsilon}_{out,bi} = \epsilon_g^0 R_g^+ + \epsilon_g^T R_g^+ - dq^b/dt, \quad V-1.4$$

where a positive value of heat input is in accord with the first law of thermodynamics for the total energy of the gas:

$$\frac{d\epsilon}{dt} = \frac{dq}{dt} - \frac{dw}{dt} \quad V-1.5$$

Next we consider the unimolecular reaction



within the element proceeding at rate  $R_g^-$  and involving the decay of  $df_{g,u} = R_g^- dt$   $g$  size clusters. The initial energy before reaction is

$$\dot{\epsilon}_{in,u} = \epsilon_g^0 R_g^+ + \epsilon_g^T R_g^+ \quad V-1.6$$

with reaction energy  $\epsilon_g^R = \lambda u^o$  we have

$$\dot{\epsilon}_g^R = -\epsilon_g^R R_g^- *$$

So

$$\dot{\epsilon}_{in,u} = \epsilon_g^0 R_g^+ + \epsilon_g^T R_g^+ + \epsilon_g^R R_g^-, \quad V-1.7$$

lib.,

The energy--after the unimolecular event--leaving the fluid element is

$$\dot{\epsilon}_{final,u} = \epsilon_{g-1}^0 R_g^- + \epsilon_{g-1}^T R_g^- + \epsilon_1^T R_g^- - dq^u/dt \quad V-1.8$$

\*having taken heat liberated within the element as positive for bimolecular reaction

Rewriting the general energy balance on the fluid element  
as

$$[\dot{\epsilon}_{out,bi} - \dot{\epsilon}_{in,bi}] + [\dot{\epsilon}_{final,u} - \dot{\epsilon}_{initial,u}] = 0 \quad V-1.9$$

and substituting Eqs. V-1.2, V-1.4, V-1.7 and V-1.8 gives

$$\left. \begin{aligned} & + (\epsilon_g^0 R_g^+ + \epsilon_g^T R_g^+ - dq^b/dt) \\ & - (\epsilon_{g-1}^0 R_g^+ + \epsilon_{g-1}^T R_g^+ + \epsilon_1^T R_g^+ + \epsilon_g^R R_g^+) \\ & + (\epsilon_{g-1}^0 R_g^- + \epsilon_{g-1}^T R_g^- + \epsilon_1^T R_g^- - dq^u/dt) \\ & - (\epsilon_g^0 R_g^+ + \epsilon_g^T R_g^+ - \epsilon_g^R R_g^-) \end{aligned} \right\} \begin{array}{l} \text{bi.} \\ \\ \\ \text{Uni.} \end{array} = 0$$

So

$$\begin{aligned} - dq^b/dt - \epsilon_{g-1}^0 (R_g^+ - R_g^-) - \epsilon_{g-1}^T (R_g^+ - R_g^-) - \epsilon_1^T (R_g^+ - R_g^-) \\ - dq^u/dt - \epsilon_g^R (R_g^+ - R_g^-) = 0 \end{aligned}$$

Defining  $dq = dq^b + dq^u$  gives

$$\begin{aligned} \frac{dq}{dt} = - \epsilon_{g-1}^0 (R_g^+ - R_g^-) - \epsilon_{g-1}^T (R_g^+ - R_g^-) - \epsilon_1^T (R_g^+ - R_g^-) \\ - \epsilon_g^R (R_g^+ - R_g^-) \end{aligned} \quad V-1.10$$

Further, if  $(R_g^+ - R_g^-) \equiv \dot{\phi}_g^n$ , or net flux on the element, Eq.

V-1.10 can be written as

$$\frac{dq}{dt} = - (\epsilon_{g-1}^0 + \epsilon_{g-1}^T + \epsilon_1^T + \epsilon_g^R) \dot{\phi}_g^n \quad V-1.11$$

where  $\epsilon_{g-1}^0 = \frac{g-1}{2} \lambda_{g-1} u_{11}^\circ$  (HSC) or  $(g-2)u_{11}^\circ$  (WCM). Conceptually,

the balance on the fluid element now appears as in Figure V-1.1.

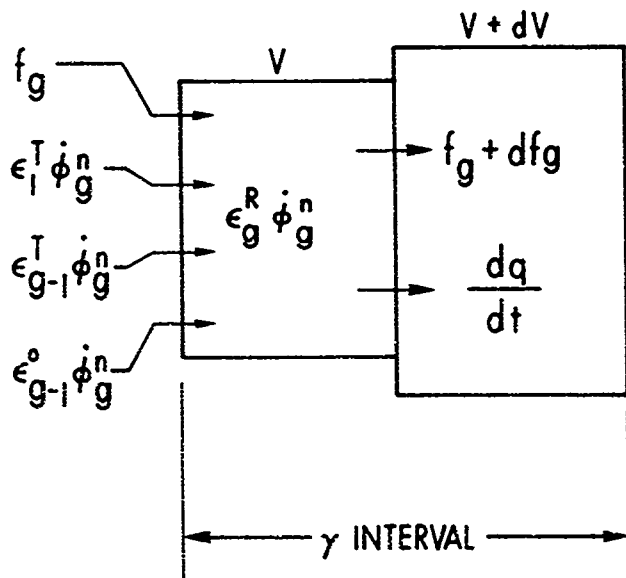


Figure V-1.1  
Computation Model



This non-stationary result for  $dq/dt$  is not related to the latent heat, an equilibrium constant pressure, temperature concept. It does define the reaction energy on net growth or decay of clusters which behave as a perfect gas and is the heat addition term in the first law, Eq. V-1.5. In a binary system such as water vapor in air, care must be taken in precisely defining the overall system described by equation V-1.5 since the heat production described by equation V-1.5 is considered as originating in an external source.

If  $C_{VO}$  is the specific heat per cc of the carrier gas, the specific heat of the mixture is

$$C_V = C_{VO} + k \sum_{g=1}^{g_\infty} \{X_g + (S_g + \zeta_g)/2\} f_g, \quad V-1.12$$

where  $f$  denotes a non-stationary concentration.

Combining Eqs. V-1.5 and V-1.11 for the constant volume cases gives for the mixture:

$$\frac{dT}{dt} = \frac{-1}{C_V} [\epsilon_{g-1}^0 + \epsilon_{g-1}^T + \epsilon_1^T + \epsilon_g^R] \dot{\phi}_g^n \quad V-1.13$$

If  $p^\circ$  and  $T^\circ$  are the pressure and temperature before quenching the perfect gas law is

$$\frac{dp}{dt} = \frac{p^\circ}{T^\circ} \frac{dT}{dt} \quad V-1.14$$

$$\text{and } p = kT (f_O + \sum_{g=1}^{g_\infty} f_g) \quad V-1.15$$

Equations V-1.13 and V-1.14 are non-integrable so that  $p$  and  $T$  must be solved for numerically from an initial equilibrium cluster distribution  $\{C_g\}$  at  $p^\circ$  and  $T^\circ$ . The pressure may be arrived at either by V-1.14 or V-1.15 where <sup>(1)</sup> (see also Table V-1.1).

$$\frac{df_g}{dt} = R_g^+ - R_{g+1}^- + R_{g+1}^- - R_g^- \quad V-1.16$$

With this set of equations one may evaluate in a step-wise manner the changes in state that occur in a constant volume containing moist air as it is quenched or heated. The temperature change produced by the entire population  $\{f_g\}$  shift is applied after calculating equation V-1.16 for all  $g$  with the same instantaneous initial conditions.

The non-equilibrium behavior of the initial stationary cluster distribution  $\{C_g\}$  described by case c, Table III-5.1 and subjected to an instantaneous temperature drop of  $0.0001^\circ\text{K}$  (the approximate average temperature drop per collision interval in later experiments) is given in Figure V-1.2. Details of performing this calculation are given in the following section and in Appendix (3); all expansion terms are simply nulled out for this constant volume case and the output is examined each calculating interval of  $0.480$  n sec. In order to gain some insight into the system behavior in the simplest case, the temperature changes indicated by equation V-1.13 (practically nil) are also suppressed after the initial quench of  $0.0001^\circ\text{K}$ .

The ordinate of Figure V-1.2 is obtained by dividing each rate  $df_g$  by the final positive value calculated for that size  $g$  (defined  $df_{1-}$ ) while the abscissa is the number  $n$  of time increments  $\Delta t \approx 0.480$  n sec. The dimer behavior is not shown because of relative magnitude; at  $n=1$ ,  $df_2 = -1.22 \times 10^{-9}$ ; at

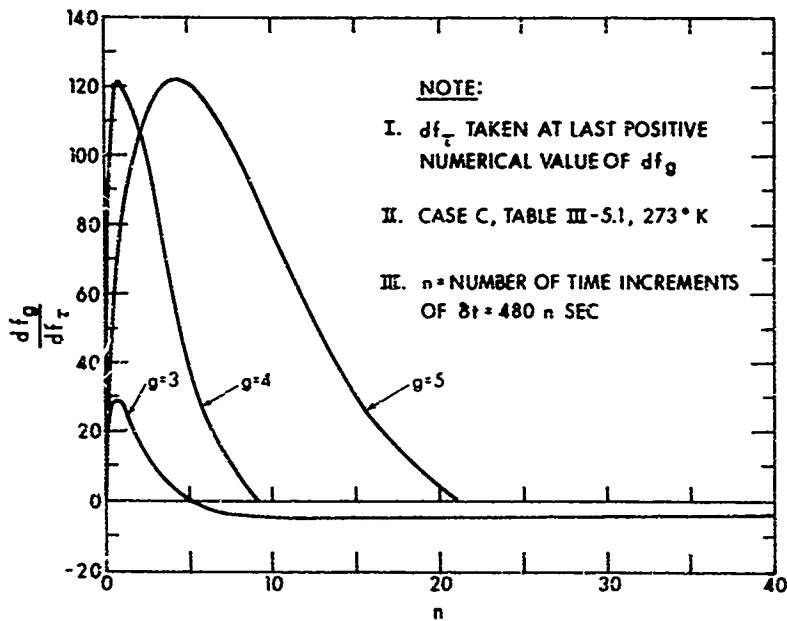


Figure V-1.2  
 Normalized Rates for Constant Volume Quench  
 $\Delta T = -0.0001^\circ \text{ K}$

$n=40$ ,  $df_2 = -0.708 \times 10^8$ . The dimer, therefore, behaves here much like a monomer since its rate is negative throughout; larger size clusters all have rates which are first positive, then negative. It will be seen later that with expansion the dimer rate is positive until departure from the adiabat occurs.

On changing  $\Delta T$  to a positive increment of  $+0.0001^\circ K$ , or a heat bath, the opposite behavior is observed (though not symmetric) with the dimer increasing throughout. The dimer literally receives a "shower" of fractured trimer leading to positive rates. If  $\Delta T$  is increased slightly to say 0.001 or 0.01, then a negative rate with the typical type of behavior for the larger cluster sizes shown in Figure V-1.2. The time to the first reversal of sign, i.e., at  $df_1$ , is given for each cluster size in Figure V-1.3 as a matter of reference.

The behavior of the cluster is evident in Figure V-1.2 with a wave-like disturbance oscillating in the medium until damped by the growth and decay processes. Interpreting the results of Figure V-1.3 as relaxation times (in attaining equilibrium) would be incorrect since gradients would still exist in the medium at the times shown.

A reassuring check on the theory and computer analysis is available at this point. Since the equilibrium solution was obtained by detailed balance involving non-equilibrium rates, the use of an equilibrium distribution  $\{C_g\}$  at temperature  $T$  in a non-equilibrium calculation for  $\{f_g\}$  at temperature  $T$  should yield stationary rates with  $R_g^+ = R_g^-$ .

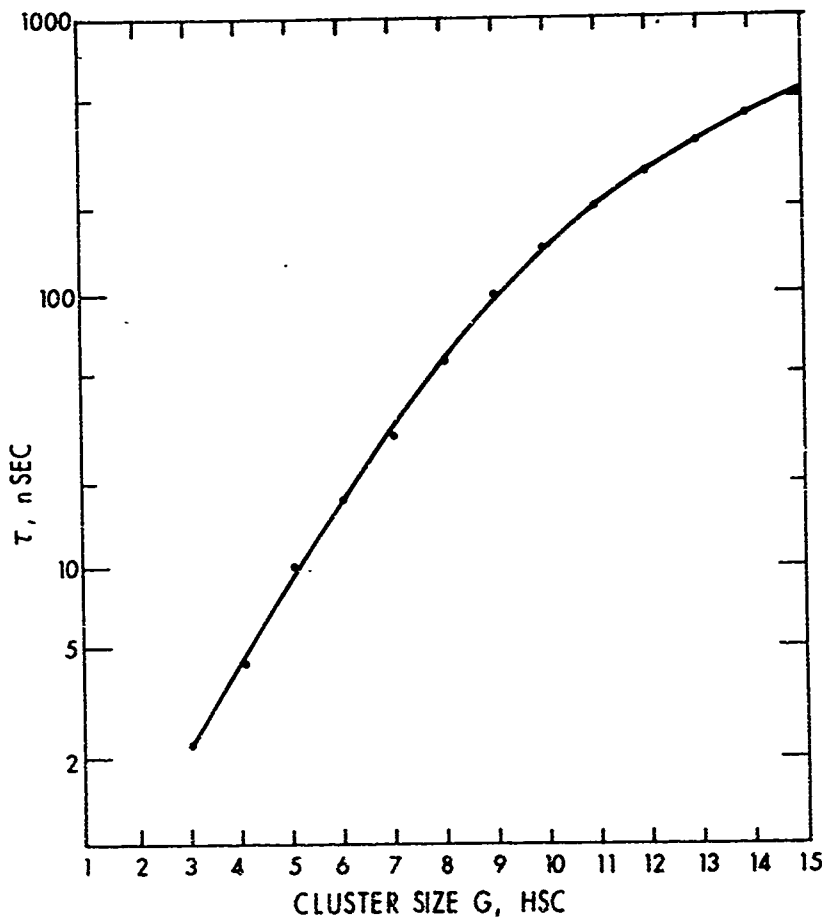


Figure V-1.3  
Reversal Times for Quench of  $\Delta T = -0.0001^\circ \text{K}$

all  $g$ . The use of hard sphere collision diameters gives a check to three digit accuracy. It was found, however, that a check to greater accuracy was possible by modifying the monomer, dimer collision cross sections, calculating the equilibrium distribution  $\{C_g\}$ , then checking for stationarity. For the hard sphere clathrate, the use of  $\sigma_{1,2} = 1.95 r_1$  (vice  $2.0 r_1$ ) and  $\sigma_{1,1} = 2.05 r_1$  (vice  $2.0 r_1$ ) gave equality in  $R_g^+ = R_g^-$  from three to five digits, all  $g$ , with the results at 273°K given in Table V-1.2.

For the constant volume quench (or heat bath) it would be possible to follow the behavior of individual clusters in attaining a new equilibrium by continuing the calculation of Figure V-1.2. If, however, a new temperature lower (or higher) by another increment of  $\Delta T$  is imposed at time  $t + \Delta t$ , it becomes impossible to interpret what is happening on an individual cluster versus time basis. This is the process occurring in a rapid expansion where the rate processes of each time increment modify those of the succeeding one. It appears fruitless to try to relate such results to relaxation times, rather, investigation of the behavior of the cluster population on the whole is more rewarding.

TABLE V-1.2  
STATIONARY GROWTH AND DECAY RATES AT 273°K

| g  | $R^+ (\text{cm}^{-3} \text{sec}^{-1})$ | $R^- (\text{cm}^{-3} \text{sec}^{-1})$ |
|----|--|--|
| 2  | $0.40966 \cdot 10^{22}$                | $0.40956 \cdot 10^{22}$                |
| 3  | $0.26336 \cdot 10^{22}$                | $0.26337 \cdot 10^{22}$                |
| 4  | $0.47028 \cdot 10^{20}$                | $0.47020 \cdot 10^{20}$                |
| 5  | $0.12430 \cdot 10^{18}$                | $0.12429 \cdot 10^{18}$                |
| 6  | $0.25205 \cdot 10^{15}$                | $0.25201 \cdot 10^{15}$                |
| 7  | $0.43719 \cdot 10^{12}$                | $0.43711 \cdot 10^{12}$                |
| 8  | $0.68725 \cdot 10^9$                   | $0.68712 \cdot 10^9$                   |
| 9  | $0.10143 \cdot 10^7$                   | $0.10142 \cdot 10^7$                   |
| 10 | $0.14395 \cdot 10^4$                   | $0.14392 \cdot 10^4$                   |

Adiabatic Expansion; Comparison with Experiment

The remaining limiting constraint, No. 6, is now considered. In the expansion of moist air in a supersonic nozzle pressure "humps" which are steady in time develop in the regions of condensation. The pressure distribution selected here for comparison is free of shock wave pressure disturbances which could be within a zone of condensation<sup>7,8,9</sup>. Consequently the entire difference in static pressure from that encountered in a moisture-free nozzle flow is due to the effects of heat addition from condensation. We know therefore that a matching

of calculated pressure with the experimentally measured pressure should be a meaningful test of the parameters involved in the theory. One further test (which is the subject of future investigation) is the prediction of other experimental results based on the parameters determined here.

Having gained some insight into possible modes of cluster behavior it is worthwhile referring to Figure IV-1.1 to define the approach used in comparing numerical calculations with experiment. For a given set of molecular parameters it is possible now to calculate conditions at saturation,  $\{C_g\}_{J=0}$ , point A', then calculate the undersaturated initial cluster distribution  $\{C_g\}_{J<0}$ , both at initial temperature  $T_{01}$ . Using  $\{C_g\}_{J<0}$  as an initial distribution it will now be possible to calculate the change in cluster concentration  $df_g$  for all  $g$ , by rate expression V-1.16 modified to include the effects of expansion. The partial pressure of the entire population  $\{f_g\}$  is then simply

$$P_v = \sum_{g>0} f_g kT \quad V-2.1$$

The objective here, therefore, is to calculate this pressure, add to it the local pressure of the carrier gas and compare the result with the static pressure obtained from experiment along the equivalent path A-B-C, Figure IV-1.1. To do this we must add to the results of the previous section the effect of expansion occurring in the flow.

For the steady inviscid expansion experiencing no body



forces the net rate of internal energy change per cc is given by V-1.5 where

$$\frac{dw}{dt} = p \frac{d(\ln v)}{dt} \quad V-2.2$$

Considering one dimensional steady flow at velocity  $u$  in a nozzle of cross sectional area  $A$ , density  $\rho$ , the mass flow rate obeys

$$\frac{d}{dt} (\rho Au) = 0, \quad V-2.3$$

and the volumetric flow rate is simply  $Au$ . The quantity  $d(\ln v)/dt$  is thus given by

$$\frac{d}{dt} (\ln v) = \frac{d}{dt} (\ln Au). \quad V-2.4$$

Since  $d \ln y/dt = 1/y \, dy/dt$ , hence

$$\frac{d}{dt} \ln Au - \frac{1}{Au} [A \frac{du}{dt} + u \frac{dA}{dt}] = \frac{d}{dt} [\ln u + \ln A] \quad V-2.5$$

Now, rewriting equations V-1.5, V-2.2 and V-2.4 and defining  $de = c_v \, dT$  gives

$$c_v \frac{dT}{dt} = \frac{dq}{dt} - p \frac{d(\ln Au)}{dt}, \quad V-2.6$$

and having  $dq/dt$  by equation V-1.6,  $c_v$  by equation V-1.12 and  $p$  by equation V-1.15 allows expressing the temperature in equation V-2.6 by

$$\begin{aligned} \frac{dT}{dt} = \frac{1}{c_v} [- \sum_{g>1} (c_{g-1}^0 + \epsilon_{g-1}^T + \epsilon_1^T + \epsilon_g^R) \dot{\phi}_g \\ - kT (f_0 + \sum_{g>0} f_g) \frac{d(\ln Au)}{dt}]. \end{aligned} \quad V-2.7$$

The pressure follows from the ideal gas law since

$$\frac{dp}{dt} = p \frac{d(\ln T/v)}{dt} = p \frac{d}{dt} (\ln T - \ln v), \quad V-2.8$$

so by equation V-2.4

$$\frac{dp}{dt} = p \left[ \frac{d(\ln T)}{dt} - d \left( \frac{\ln Au}{dt} \right) \right], \quad V-2.9$$

or combining equations V-2.9 and V-2.7 allows

$$\begin{aligned} \frac{d \ln p}{dt} = & \frac{1}{C_v T} \left[ - \sum_{g>1} (\epsilon_{g-1}^0 + \epsilon_{g-1}^T + \epsilon_1^T + \epsilon_g^R) \dot{\phi}_g^n \right. \\ & \left. - \left[ 1 + \frac{k}{C_v} (f_o + \sum_{g>o} f_g) \right] \frac{d(\ln Au)}{dt} \right] \end{aligned} \quad V-2.10$$

Here again equation V-2.7 and V-2.10 are non-integrable and numerical solution is necessary. As in the constant volume case the pressure may be found from equation V-1.15 rather than from V-1.14.

One further consideration is needed to complete the description of the expanding medium. Since the volume of the system varies with time, a term

$$- f_g (d/dt) \ln V \quad V-2.11$$

must be added to eq. V-1.16, while for the diluent gas we have

$$- f_o (d/dt) \ln V, \quad V-2.12$$

noting that the volume change is already specified in terms of the area and local flow velocity in eq. V-2.5. The change in concentration of any cluster size during expansion is thus written as the sum of Eqs. V-1.16 and V-2.11

$$\frac{d\dot{\phi}_g}{dt} = (R_g^+ - R_{g+1}^- + R_{g+1}^- - R_g^-) - f_g \frac{d}{dt} (\ln V). \quad V-2.13$$

For the monomer rate equation, we have (constant volume)

$$df_1 = - \sum_{g=2}^{\infty} g \left( \frac{df_g}{dt} \right) dt, \quad V-2.14$$

or with expansion

$$df_1 = - \sum_{g=2}^{\infty} g \left( \frac{df_g}{dt} \right) dt - f_1 \frac{d}{dt} (\ln V). \quad V-2.15$$

Adiabatic expansion of moist air in a supersonic nozzle can now be examined. The case considered here (Exp. 405, Ref. 8) is free of pressure discontinuities from shock waves so the only deviation of static pressure from that of a dry adiabatic expansion is that caused by the heat input of condensing vapor. The information required of the experimental conditions for input to the numerical calculations is the initial pressure, temperature, the nozzle profile, i.e., the area  $A_{(x)}$  and slope  $dA/dx$ . In order to know the time per data interval the flow velocity  $u_{(x)}$  in the nozzle is required; this follows from solution of the equations of motion<sup>(7,8)</sup>. Inputs from the equilibrium theory<sup>(1)</sup> are the initial cluster distribution  $\{C_g\}$  and the accompanying parameters (Say case c, Table III-5.1). The objective is to match the pressure deviation in the nozzle observed at onset of condensation-- thus satisfying limiting constraint (6):

The FORTRAN computer program for calculating the non-equilibrium rates of change of cluster concentration, the temperature, pressure and other parameters is described and given in Appendix 3; the general flow chart is also given.

In essence the program calculates the rates of growth and decay for each cluster size from the dimer upwards in each calculating interval thus giving the concentration of each species with respect to time (or location). The static pressure reported is thus the sum of the partial pressures of all species present, from the monomer upwards and the carrier gas.

The calculating interval used requires further consideration. The earlier discussion on cluster behavior under constant volume-quench conditions showed that time increments on the order of the collision interval were required in that case. With the complication of expansion the interval to be used was uncertain; the minimum was still the collision interval but perhaps a longer one could be used to conserve computer time.

Collision time corresponding to the mean free path is calculable from the collision numbers of the theory<sup>(1)</sup>, i.e.:

$$\tau_g = (Z'_{og} + Z'_{lg})^{-1}, \tau > (\bar{v})^{-1} \quad V-2.11$$

where

$$Z'_{og} = Z''_{og} f_o$$

$$Z'_{lg} = Z''_{lg} f_l$$

and

$$Z_{x,g} = \left( \frac{8\pi kT}{u_{x,g}} \right)^{1/2} \sigma_{x,g}^2, \quad x = 0,1$$

Using concentrations from typical calculations we find, for example, that at 270°K,  $\tau_{10} \sim 4\text{nsec}$ . This dictates a scheme of variable step size which is described further in Appendix 3.

There appears to be no significant difference in results, however, between a constant step size and a variable step size. It is possible by this method of variable step size, though, to reduce computer time from about 16 hours per solution to about 1.5 hours. A step size twice the largest collision interval will lead to an unstable numerical solution.

A further area requiring clarification is the experimental input data. For the case considered here data on Area, Velocity, etc. were for 0.1 cm intervals. This is too coarse and must be refined; simple linear relations were used between data intervals.

A final point of clarification concerns the initial cluster distribution. Referring back to Figure IV-1.1, moist atmospheric air entered the experimental apparatus in condition A. Some expansion already occurred at the point where experimental pressure was first measured. The temperature had already dropped to 273°K at this point from 295.8°k. To account for the change in cluster concentration from point A to B, two approaches were tried.

First, the undersaturated distribution at A was calculated and expanded adiabatically to 273°K considering the absolute number of each species to remain unchanged (frozen equilibrium). Second, the equilibrium distribution at 273°K was calculated. Inasmuch as the first method gave vapor pressures slightly lower than those on the adiabat, Figure IV-1.1, the second condition was used as the initial condition in the results

reported here. There was very little difference in the two distributions and both would give nearly similar final results except that the first case would follow a path just under the adiabat.

A bit of historical development is injected at this point to show how the final solution was attained. In evaluating numerical results, initially, the greatest confidence was placed in the results of the rate equation, V-1.12. The argument stemming from the fact that  $\{C_g\}$  and  $\{f_g\}$  are closely related through detailed balance at equilibrium; with most of the experience gained in the many variations of  $\{C_g\}$ . From this the mass fraction of "condensate" is defined by considering the evolution of all clusters from the dimer upwards. The mass fraction of water clusters per kg of air is obtained by

$$X = \frac{m_1 \cdot 10^{-3}}{m_0} \sum_{g>1} \frac{g f_g}{f_0}, \quad V-2.12$$

where  $m_1$  and  $m_0$  are the mass per monomer and mass per air molecule (avg) respectively; the initial value of  $X \approx 0.006$  being neglected. If this expression is summed to include the monomer, the mixing ratio (sometimes called the specific humidity) is obtained,

$$X_1 = \frac{m_1}{m_0} \cdot 10^{-3} \sum_{g>0} \frac{g f_g}{f_0} \quad V-2.13$$

$X_1$  should remain constant throughout equal to the initial value, here equal to 4.86 g/kg. This is in effect another internal boundary condition to be satisfied.

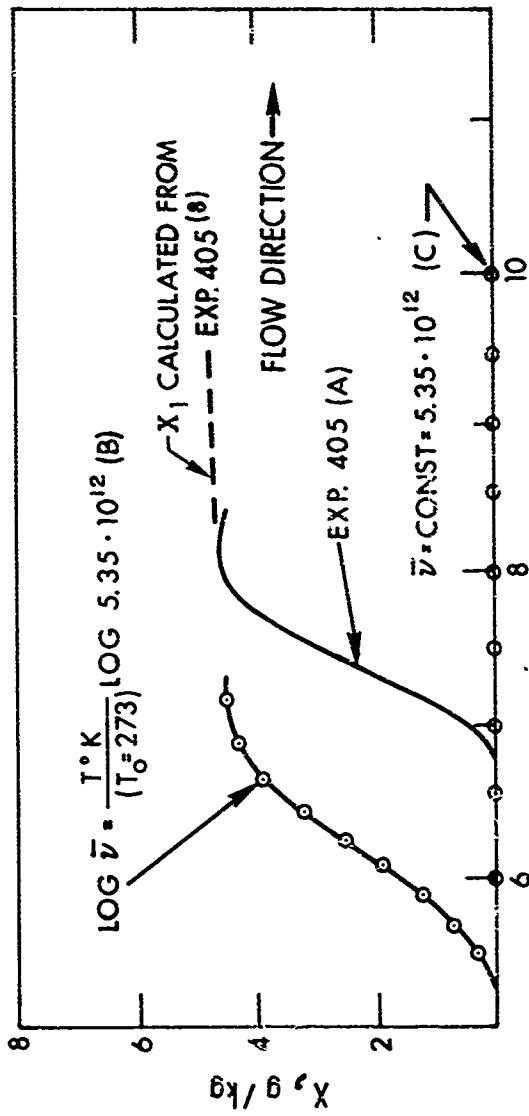
The basis of comparison for  $X$  is the result of solution of the equations of motion for the flow and given elsewhere<sup>7,8</sup>. Although this earlier solution relies on the use of macroscopic latent heat and therefore has limited validity with respect to the condensate mass fraction, it does appear to be a useful first approximation and is plotted for experiment #405 in Figure V-2.1. Some early results for  $X$  are given in Figure V-2.1.

An interesting problem is encountered at this point, namely, the strong dependence of  $X$  on  $\bar{v}$ . If case c, HSC, Table III-5.1 is used, curve (c) results which is quite disappointing in that little or no condensate appears; the small amount appearing is late in time or downstream of experimentally observing results. If a temperature dependence is imposed on  $\bar{v}$ , say

$$\log \bar{v} = \frac{T}{T_0} \log 5.35 \cdot 10^{12}, \quad \text{V-2.14}$$

with  $T_0 = 273$ , still satisfying case (c) Table III-5.1, then curve (B) results which is premature or upstream of observed results.

At this point an intense investigation was made on the influence of other parameters in the theory as well as different initial condition (Table III-5.1). Referring to the rate expression in Table V-1.1 one finds that for curve (c) the decay rates are too large and the system evolution is incomplete by the time the nozzle exit at  $l = 9$  cm is reached. Parametric



X, cm.

Figure V-2.1  
Condensate Mass Fraction, HSC



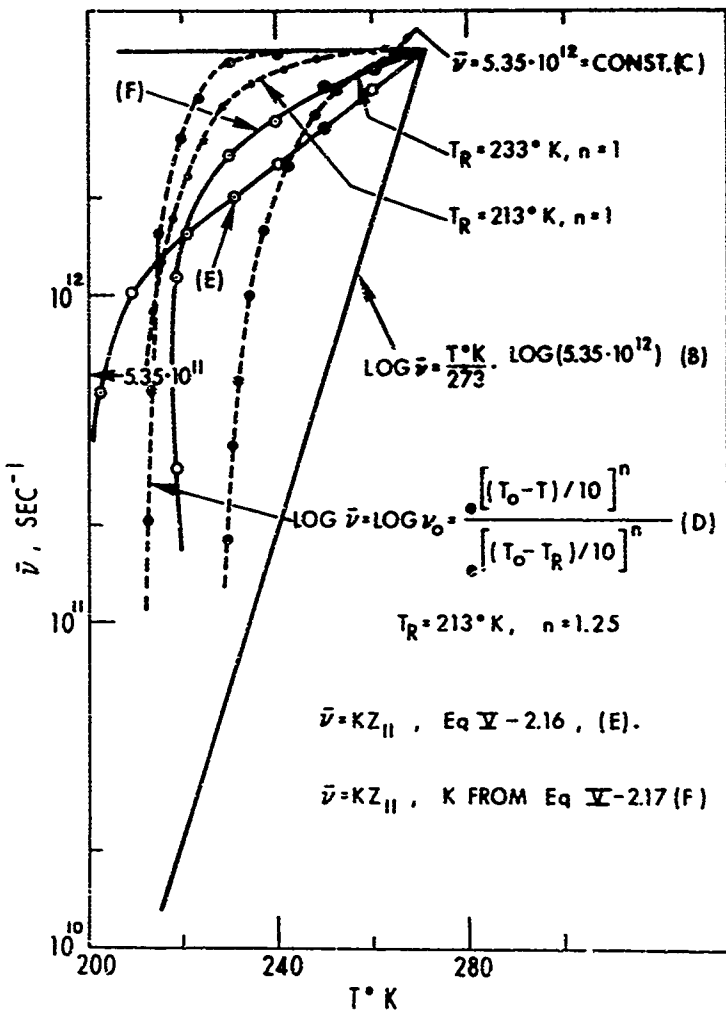


Figure V-2.2  
Behavior of Internal Circulation Frequency

studies showed there was little possibility that variation of  $u_{11}$ ,  $\gamma$ ,  $v_{01}$ , etc. could substantially affect the system evolution so attention was turned to  $\bar{v}$ .

It appeared now that the frequency  $\bar{v}$  was the dominant parameter involved. Examination of Figure V-2.2 shows some of the variations of  $\bar{v}$  that were considered, with curve (c) and (b) corresponding to those in Figure V-2.1. Since the experimental results appeared to be bracketed by curves (C) and (B), intermediate variations for  $\bar{v}$  were considered with the following yielding the most promising results (curve D)

$$\log \bar{v} = \log v_0 - \frac{\exp[(T_0 - T_i)/10]^n}{\exp[(T_0 - T_R)/10]^n} \quad \text{V-2.15}$$

Having gained some insight into the nature of the behavior of the theory's parameters attention was shifted to comparison of numerical results with the actual experimental pressure distribution. Figure V-2.3 shows the degree of comparison in static pressure (dimensionless  $p/p_{01}$ ) when  $n = 5/4$  and  $T_R = 213^\circ\text{K}$ , keeping in mind that the calculations were initiated at  $T = 273^\circ\text{K}$  at  $X = 1.5$  cm. The isentrope is followed numerically as is the experimentally observed pressure deviation. The result in Figure V-2.3 for  $X$  was expected to differ from the earlier result as pointed out previously because of the earlier use of latent heat.

Once the close match in pressure was achieved reexamination of parameters in the theory showed nearly direct proportionality

between  $\bar{v}$  and collision number  $Z_{11}$  for the monomer-monomer interaction. If fact allowing

$$\bar{v} = k Z_{11} \quad \text{V-2.16}$$

gave a match in static pressures within a few percent. A small variation in  $k$  (from  $2.05 \times 10^{-12}$  to  $1.21 \times 10^{-12}$ ) with temperature and saturation according to

$$k = - 7.431 - 0.0789 s + 9.54 \frac{T}{T_0}, \quad \text{V-2.17}$$

yielded a pressure distribution nearly identical with experiment. (See Figure V2.3).

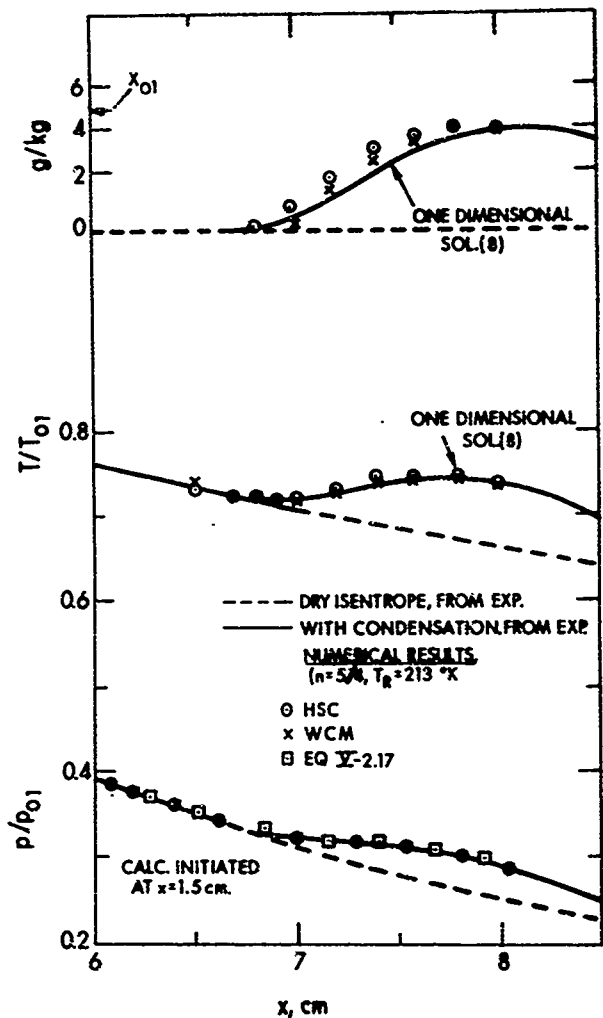


Figure V-2.3  
 Comparison of Present Results with Experimental  
 Pressures and Earlier One-Dimensional Calculations

## VI. COMPLETE EQUILIBRIUM AND NON-EQUILIBRIUM SOLUTIONS

### 1. Cluster Behavior

We summarize here the results obtained for both the HSC and WCM, case (C) and (e) Table III-5.1 as modified by  $\bar{v}$  in equation V-2.15. A complete equilibrium iteration to satisfy all limiting constraints requires less than an hour at an interactive computer terminal (GE-H635) while a single non-equilibrium solution on a fixed collision interval basis requires about 15 hours of actual computer time (CPU) on a medium scale computer (PDP 15/40). This is reduced to about 1.5 hours by using variable collision interval basis described earlier and in more detail in Appendix 3. As any computed parameter is observable on an individual cluster size basis at any time, calculations were limited to size  $g=10$  after observing virtually no numerical contribution to the results (i.e.  $p$ ,  $T$ ,  $X$ ) above a cluster size of  $g=8$ .

Initial conditions for both the HSC and WCM case at 273°K (saturated equilibrium condition) are given in Table VI-1.1. The evolution of the cluster populations from the initial condition  $\{C_g\}_0$  of Fig. IV-1.2 is given in Fig. VI-1.1 through VI-1.4. Recalling that the principal differences between both the classical HSC and the water model lie in the structure,  $\eta_g$ , the collision cross section  $\sigma_{1,g}$  and the nearest neighbor parameter  $m_\lambda$  one finds identical results for static pressure and close agreement for temperature and condensate  $X$ . Also the larger WCM cross section tends to shift the hump in the

TABLE VI-1.1  
INITIAL CONDITIONS, SATURATED EQUILIBRIUM, 273°K

| Size<br>g | HSC<br>C <sub>g</sub> | WCM<br>C <sub>g</sub> |
|-----------|-----------------------|-----------------------|
| 1         | 0.16000000E+18        | 0.16000000E+18        |
| 2         | 0.10299099E+15        | 0.10299099E+15        |
| 3         | 0.37137217E+13        | 0.37137317E+13        |
| 4         | 0.60239349E+11        | 0.14863239E+12        |
| 5         | 0.47734832E+09        | 0.29168346E+10        |
| 6         | 0.20353456E+07        | 0.30693876E+08        |
| 7         | 0.62537311E+04        | 0.23091140E+06        |
| 8         | 0.15731362E+02        | 0.14066905E+04        |
| 9         | 0.34735999E-01        | 0.74236071E+01        |
| 10        | 0.70293203E-04        | 0.35375547E-01        |
| 11        | 0.13420118E-06        | 0.15648930E-03        |
| 12        | 0.24676055E-09        | 0.65534307E-06        |
| 13        | 0.44375285E-12        | 0.26360155E-08        |
| 14        | 0.78974221E-15        | 0.10297684E-10        |
| 15        | 0.14039987E-17        | 0.39412301E-13        |

distribution outward from g=4, HSC to g=6 WCM; the concentration of larger sizes being higher in the latter case. If, for example,  $n_{WCM}$  is used with  $\sigma_{HSC}$ , the static pressure and temperature calculated is about 5% lower than experimental. The disappearance of the smaller sizes, akin to Ostwald ripening is also accentuated in the WCM case. Once the zone of observed condensation (here  $x \approx 7.0$  cm) is reached the smaller sizes (g=2,3, HSC) begin disappearing, i.e.  $df_g < 0$ ; for the WCM this applies to sizes through g=5.

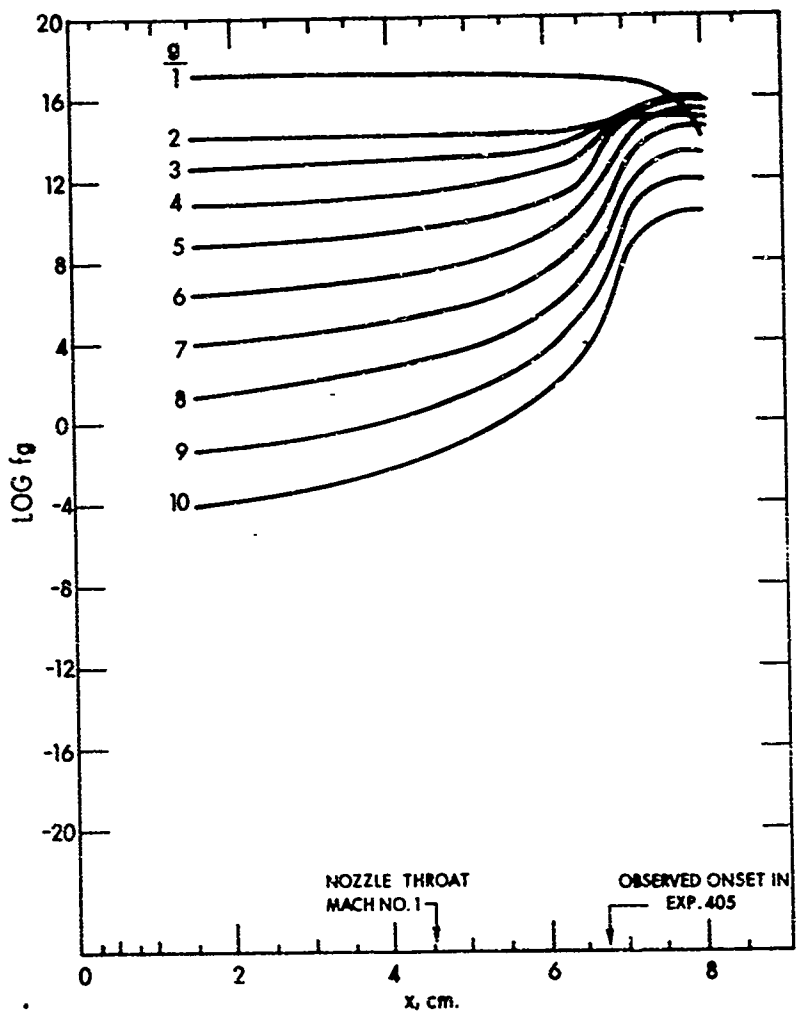


Figure VI-1.2  
 Variation of Cluster Concentration with  
 Nozzle Location, HSC

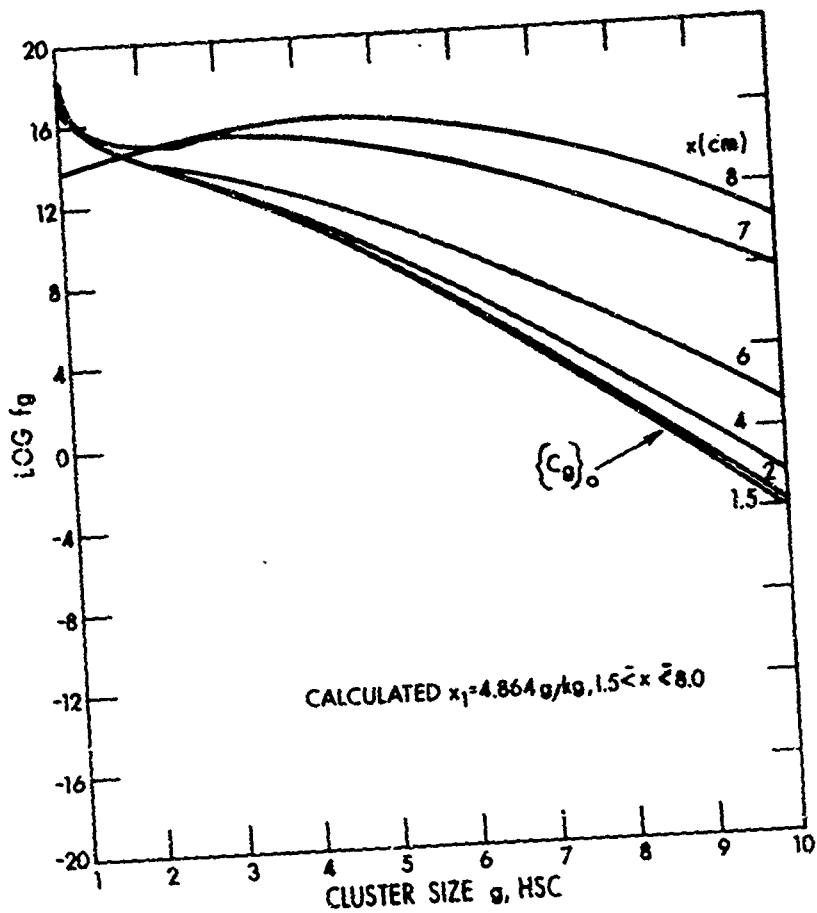


Figure VI-1.1  
 Variation of Cluster Concentration  
 with Size, HSC



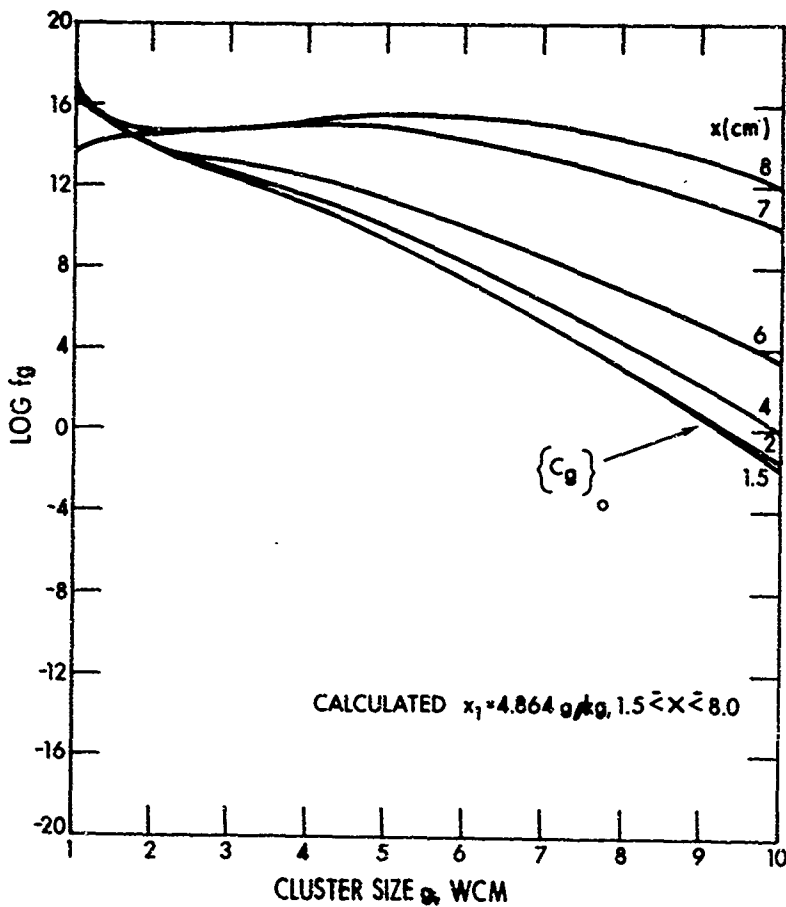


Figure VI-1.3  
 Variation of Cluster Concentration  
 with Size, WCM

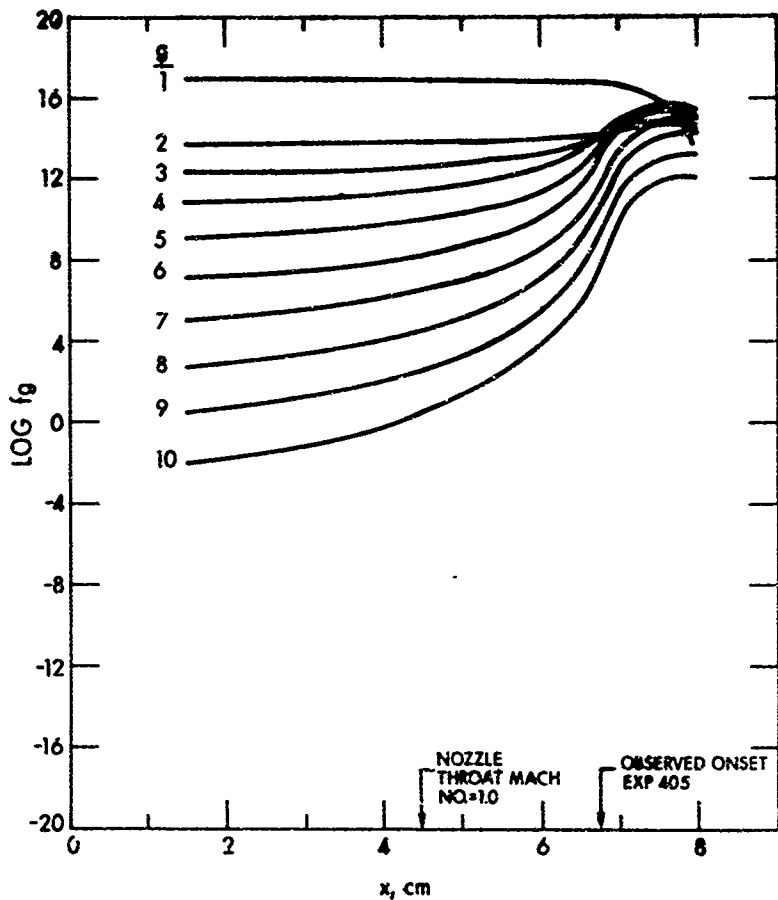


Figure VI-1.4  
 Variation of Cluster Concentration with  
 Nozzle Location, WCM

## 2. Gas Phase Metastable Equilibrium

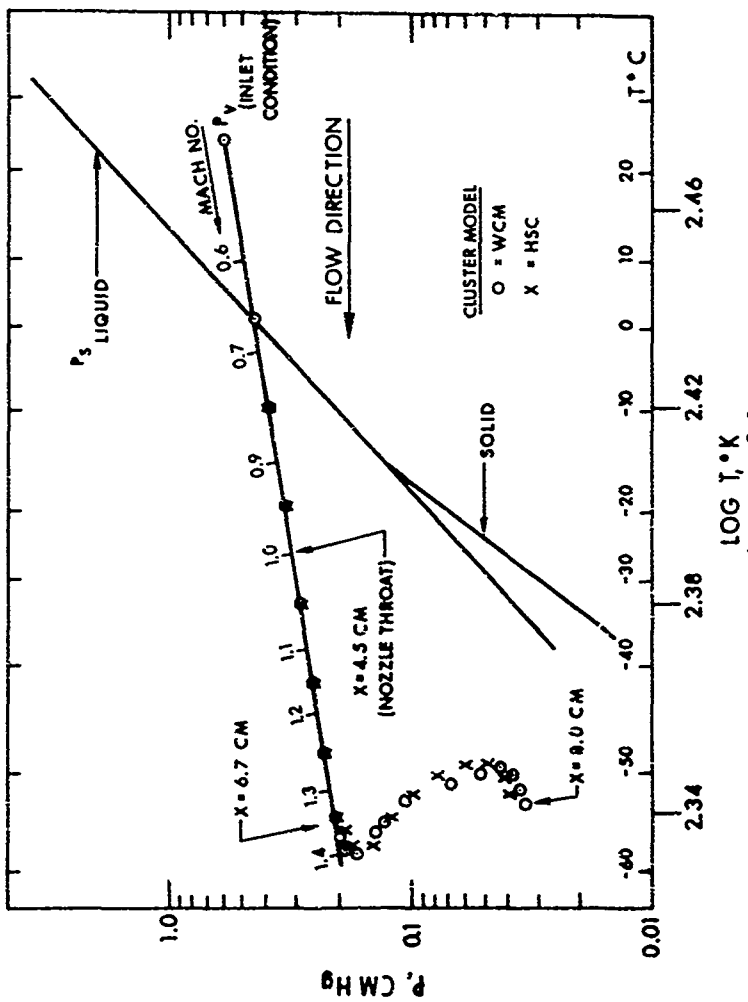
In Figure IV-1.1 the general expected path of the adiabatic expansion up to onset was described. Now, having satisfied all limiting constraints (1-6) a final check on the solution is to observe whether the adiabatic path up to onset is calculated and mass balance maintained.

Figure VI-2.1 gives the path calculated for both the HSC and WCM with calculated results falling on the adiabat for the carrier gas ( $C_p/C_v = 1.4$ ); the flow Mach no. is also plotted. The vapor pressure given is calculated from

$$P_v = \sum_{g>0} kTf_g \quad \text{VI-2.1}$$

Although the calculated pressure for  $4.5 < x < 6.7$  indicates that equilibrium pressures are attained, the expanding mixture is not in true thermodynamic equilibrium since the gradients indicated, for example in Fig. VI-1.1, preclude equilibrium. Were sufficient time available for the system to evolve to equilibrium for  $4.5 < x < 6.7$ , metastable cluster distribution as in Fig. IV-1.2 would exist (or conversely, if the rates were sufficiently rapid).

The results of this calculation indicate that metastable equilibrium is not attained in the course of the moist air expansion considered here (exp. 405)<sup>(8)</sup> in spite of the presence of equilibrium vapor pressure. The vapor pressure up to onset is a result of the monomer partial pressure which follows the expansion hardly affected by cluster growth until onset as is evident in Figs. VI-1.2 and VI-1.4. Fig. VI-2.1



indicates the vapor pressure from experimental inlet condition to  $x = 8.0$  cm. While interpreting the results after onset ( $x=6.7$ ), it should be noted that the temperature increases due to the heat of reaction by about  $24^\circ\text{K}$  over the dry isentropic temperature. Over the course of the entire calculation the mixing ratio or specific humidity remains constant at  $x_1 = 4.864$  g/kg indicating conservation of mass throughout. The path beyond  $x=8.0$  is then again dominated by the continuing expansion of the carrier gas along another adiabat (GFE, Fig. IV-1.1; the process could be interpreted as an expansion with modified initial conditions. That other nozzle expansions behave in this manner is evident by the pressure curve envelope after onset <sup>7,8</sup>.

It has generally been assumed in the past that onset of condensation is associated with collapse of metastable equilibrium; this would mean transition from a metastable supersaturated cluster distribution, Fig IV-1.2 to a saturated cluster distribution, III-6.1. The condensate would then be the difference in the quantity  $m_1 \int g_1 g_c$  with the latter distribution falling below the former.

Were the reactions in our expansion sufficiently fast, the metastable supersaturated distributions of Fig. IV-1.2 would be obtained. It is seen, however, in the non-equilibrium evolution in Figures VI-1 through 4 that the metastable distribution of Fig. IV-1.2 are not attained - - - but since the calculated vapor pressure equals that predicted

by the equilibrium isentrope up to onset point in Fig. VI-2.1 the vapor would be assumed to be in metastable equilibrium. We see therefore that the metastable concept applies to vapor pressure and supersaturation but not to cluster distribution.

By the results of Figs. VI-1.2 and VI-1.4 we can interpret onset of condensation either in terms of monomer and associate departure from metastable vapor pressure with disappearance of the monomer or alternatively in terms of the entire cluster population upwards from the dimer. In terms of the monomer-onset is the 'collapse' of the metastable vapor pressure, in terms of the rest of the cluster population--onset is not collapse of the metastable cluster distribution (it never having been attained) but sudden growth caused by decrease in the cluster decay rates. This decrease is a direct result of the decrease in internal circulation frequency  $\bar{v}$ .

It appears from these calculations that the existence of the gas phase metastable vapor pressure, i.e. when  $J > 0$ , is directly related to both the rates of growth and decay  $R^+$ ,  $R^-$  on one hand, and to  $\bar{v}$  on the other. It also appears that  $\bar{v}$  may be related to the relative abundance of monomer by Equation V-2.16. When sufficient time has elapsed in an expansion for the cluster concentrations to have grown due to the continual 'quench' and consequently the increased rates  $R^+$ ,  $R^-$  have begun to affect the monomer concentration, then the decrease in monomer concentration causes the frequency  $\bar{v}$

to decrease which further accelerates the process as  $R^-$  is proportional to  $\bar{v}$  and  $R^- \ll R^+$ . The net effect is the release of an enormous amount of energy in a short time with the temperature gradient of the flow changing to about  $5 \times 10^5$  °K/sec. from about  $-5 \times 10^5$  °K/sec.

### 3. Possible Water Cluster Structures

The very nature of the cluster theory <sup>(1)</sup> originally developed for monomolecular vapors allows little detail or description of molecular structure. This attempt in applying the theory to a more complicated species like  $H_2O$  is encouraging especially since only an average or effective value of pair interaction energy  $u_{11}^\circ$  is required but it raises the question of the behavior of the circulation frequency  $\bar{v}$ . Assuming that the  $\bar{v}$  question is resolved then it appears that the limiting constraints developed here allow extension of the theory to other than monomolecular vapors.

A composite summary of both the hard sphere collision and the water clathrate model is given in Table VI-3.1 and Figs. VI-3.1 and VI-3.2. It should be recalled that  $c_g = 1$  for  $g \leq 20$  for both HSC and WCM which implies that all molecules in this size range of clusters are surface sites.

Inasmuch as the theory <sup>(1)</sup> is based on classical interpretation of intermolecular forces, the HSC case is in keeping with this concept. A conceptual view of HSC clusters, up to  $g=7$  is given in Fig. VI-3.1 with an attempt to represent  $n_g$ , the number of bonds and  $\lambda_g$ , the number of nearest neighbors (taken here as the average).

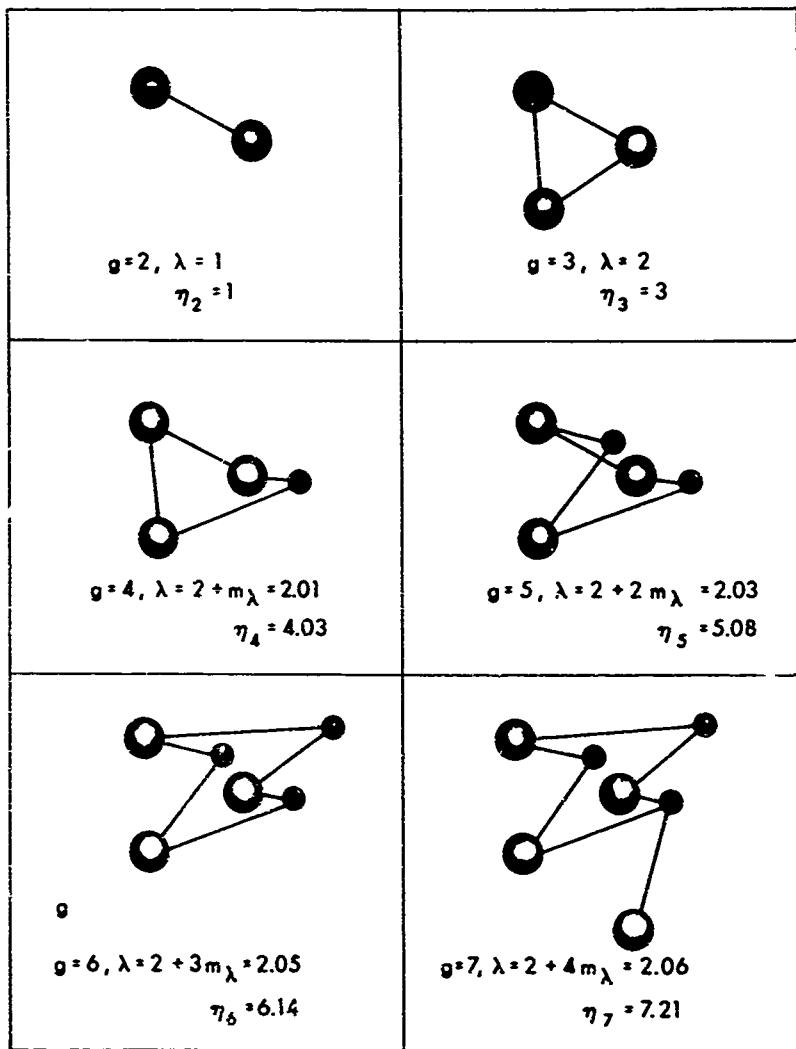


Figure VI-3.1  
Interpretation of Structure, HSC



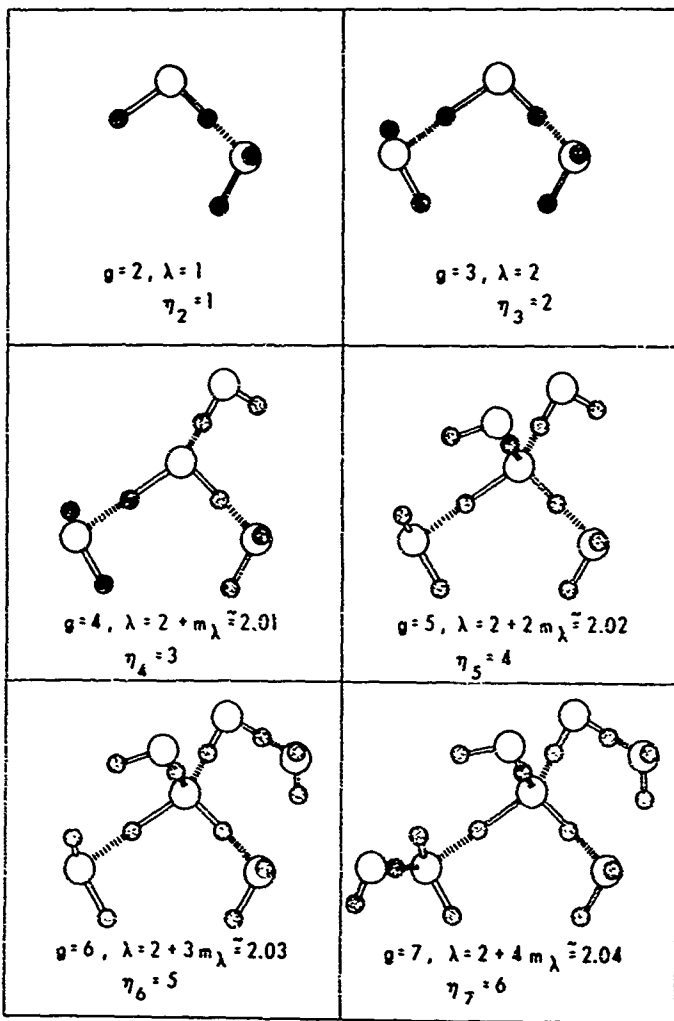


Figure VI-3.2  
Interpretation of Structure, WCM

TABLE VI-3.1  
HSC, WCM SUMMARY

| Case | $u^{\circ} \text{H/k}$ | $u^{\circ} \text{H} (\text{Kcal/mole})$ | $\bar{v}_{273^{\circ}\text{K}}$ | $\lambda_{\infty}$ | $g_{\infty}$ | $m_{\lambda}$ | $\eta_g$        |
|------|------------------------|---|---------------------------------|--------------------|--------------|---------------|-----------------|
| HSC  | 1460                   | 2.90                                    | $5.35 \cdot 10^{12}$            | 3.9                | 124          | 0.0153        | $g_{\lambda}/2$ |
| WCM  | 1460                   | 2.90                                    | $5.35 \cdot 10^{12}$            | 3.9                | 195          | 0.0097        | $g-1$           |

The WCM requires some imagination as the linear variation of  $\lambda_g$  is still allowed but  $\eta_g$  is based on the structural model of Fig. VI-3.2. Recall that  $\lambda_g \rightarrow \lambda_\infty$  as  $g \rightarrow \infty (g_\infty)$ ; here  $\lambda_\infty = 3.9$  at  $g \cong 195$ . Although, as pointed out earlier in III-4, numerous assumed variations of  $\lambda_g$  were allowed, none other than the present linear case of  $\lambda = 2$  at  $g = 3$  to  $\lambda_\infty$  satisfied limiting constraint (1-6). In the absence of theoretical prediction of  $\lambda$ , little more can be said.

Although  $\eta_g$ , WCM differs from  $\eta_g$ , HSC only by approximately unity, this difference is significant as appreciable energy is associated with the bonding (or potential energy) term in the reaction described by equation V-1.11.

It is gratifying to find that the parameters determined by the series of iterations required to satisfy limiting constraints (1-6) do, in fact, resemble those of water, especially since the value of pair interaction energy  $u_{11}^\circ$ , HSC and WCM, agrees with recent results for an average value of 2.9 kcal/mol-bond. <sup>(10)</sup> This average result is deduced from molecular dynamics calculations where the detailed structure of  $H_2O$  was realistically defined. The point is also made in the molecular dynamics study <sup>(10)</sup> that it is legitimate, to use the concept of a pairwise additive potential in lieu of an 'exact' potential for water, *provided* the pair functions are *effective* pair potentials.

## VII. COMPARISON WITH CLASSICAL THEORY

### 1. Nucleation Rates with Present Surface Tension

Earlier attempts<sup>(8)</sup> to compare the predictions of classical nucleation theory with rapid nozzle experimental results were partially successful with later studies reviewed more recently.<sup>(9)</sup> These studies have in common first, the application of isothermal equilibrium nucleation theory for 'birth' rates of critical size nuclei in highly dynamic supersonic expansions ( $\Delta T/\Delta t = -10^5 \text{ }^\circ\text{Ksec}^{-1}$ , or more). Second, one is always faced with assigning the surface tensions of clusters of extremely small size of undetermined state (liquid, solid). And, thirdly, one must choose a growth law for clusters after their 'birth' together with an attendant condensation or 'sticking' coefficient.

As is evident<sup>(8,9)</sup> some degree of success is possible using the classical approach, however, little progress can be made in interpreting the dynamical aspects of phase change, in understanding the metastable state or, in fact, predicting a priori the outcome of a new physical situation.

Keeping in mind the earlier arguments of Sections V-2 and VI-2 with regard to attainment of metastable equilibrium, the earlier calculations<sup>(8)</sup> are repeated here using the surface tension corresponding to the minimum in  $\{C_g\}$  found in Fig. IV-1.2. Plotting that value of  $g \equiv g^*$  at the minimum in  $\{C_g\}$  and the corresponding surface tension  $\Gamma(g^*)$ , gives the result in Fig. VII-1.1 with

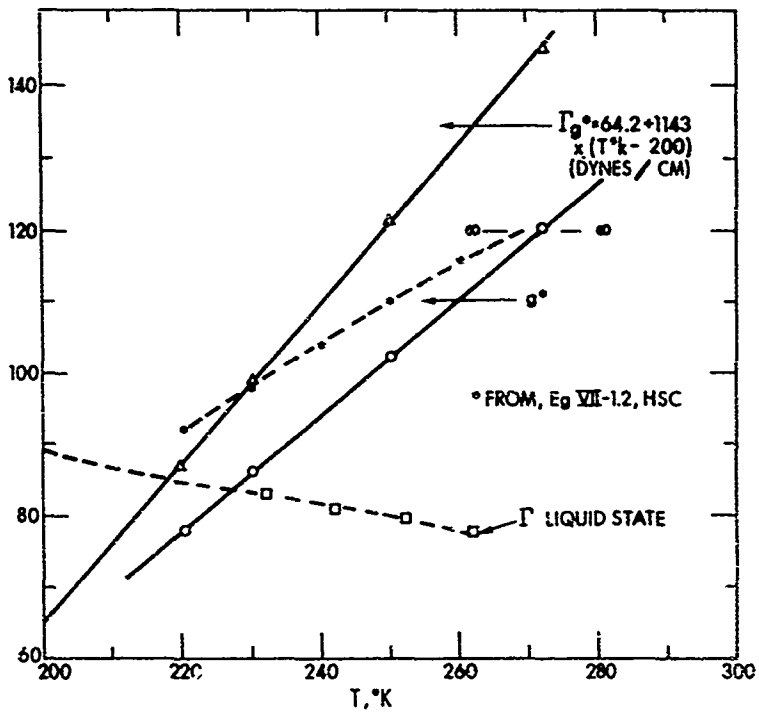


Figure VII-1.1  
 Surface Tension of Clusters if  
 Metastable Equilibrium were Attained

$$\Gamma_{g^*} = 64.2 + 1.143(T-200) \text{ (dynes/cm)} \quad \text{VII-1.1}$$

An approximate relation for  $g^*$  derivable from the theory <sup>(1)</sup> is

$$g^* = 3 + (\lambda_\infty - \lambda_3 - \frac{J}{\sigma}) \frac{1}{m_\lambda} \quad \text{VII-1.2}$$

which is plotted in Fig. VII-1.1. The approximation diverges from exact values with increasing supersaturation or decreasing temperature. At saturation, however, the parameter  $J = \ln c_1 / c_{1s} = 0$  and the approximation converges to the value required by limiting constraint (5),  $\frac{\Delta \zeta}{g \rightarrow g_m} = 0$  this is true for both the HSC and WCM!

Again, recall that our present calculations indicate metastable cluster distributions are not attained during rapid expansion yet classical nucleation theories predict the rates for metastable equilibrium corresponding to the minimum at  $C_g^*$ . Thus it is not surprising that repeating the earlier calculations <sup>(7)</sup> with the value of surface tension given by equation VII-1.1 gives little if any improvement over previous results.

In Fig. VII-1.2 typical results are given for predictions of onset of earlier experiments. <sup>(7,9)</sup> It is possible to iterate and converge numerically on experimental onset by parametric variation for, say, experiment 405. Using the iterated parameters in predicting the location of onset for experiments 416 and 295 with considerably different supersaturation yields disappointing results.

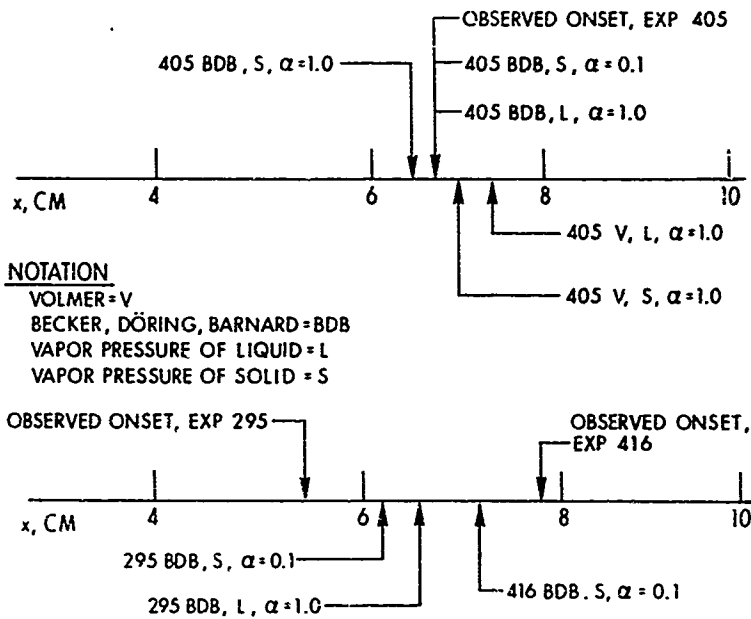


Figure VII-1.2  
 Location of Condensation Onset by Classical Nucleation  
 Rates with Metastable Values of Surface Tension

The conclusion one can draw is that classical nucleation theory should not be invoked unless the time scale of the experimental situation is long with respect to time of evolution of the metastable state. Further investigation of relaxation aspect of the present theory<sup>(1)</sup> may yield criteria on the time of evolution of the metastable state.

## 2. Future Work

In order to apply the experience gained with water vapor to predicting other water vapor experiments, further investigation of the circulation frequency  $\bar{\nu}$  is required. If, in fact,  $\bar{\nu} = (Z_{11})$  then other experiments should be predictable from the parameters given here.

Reflection on the results presented raises a question needing further investigation of the net effect on the heat of reaction of the distinct approach used in Ref. (1) in arriving at the dimerization rate in contrast to that for larger sizes. The partition function is used in the first case, consequently accounting for the zero point energy while in the latter case it is not included. If the enthalpy change of reaction were calculated it would be complicated by this fact.

An obvious extension of this work should be to nozzle expansions of a monomolecular gas such as argon as well as to other species with molecular properties susceptible to forming clathrate structures, i.e.  $H_2S$ ,  $H_2O$ ,  $CO_2$ ,  $SO_2$ , etc. although argon itself might form clathrates.



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APPENDIX 1, NOMENCLATURE

| <u>SYMBOL</u> | <u>VARIABLE</u> | <u>REMARKS</u>                     |
|---------------|-----------------|------------------------------------|
| A             |                 | *Eq. 8.8+1, Ref 1<br>2nd term      |
| ALPHA         | $\alpha_g$      | Surface to volume<br>parameter     |
| ALPHA G       | "               | *Surface to volume<br>parameter    |
| ALPPl         | $\alpha_{g+1}$  |                                    |
| AREA          | A               | Nozzle cross sec-<br>tional area   |
| AREA-MG       | A               | Sub-interval area                  |
| BIGG          | G               | *Eq.8.9, Ref 1,<br>also Appendix 4 |
| BIGM          | M               | *Eq. 8.4, Ref 1                    |
| BIGM2         | "               | "                                  |
| BK            | k               | *Boltzman constant                 |
| BRCFG         |                 | $\Gamma(3g - (\xi_g + \xi_g))f_g$  |
| C             | $C_g$           | *Equil. concentration              |
| CF            |                 | *Conversion Factor                 |
| CHJG          | $\chi_g$        | Vibrational degrees<br>of freedom  |
| CHI           | $\chi_g$        | * "                                |
| CHIGM1        | $\chi_{g-1}$    |                                    |
| CHIGPl        | $\chi_{g+1}$    |                                    |
| CHI1          | $\chi_1$        |                                    |

\*Symbols for equilibrium solution that differ from nonequilibrium solution.

|        |                 |  |
|--------|-----------------|--|
| CKP    |                 | *Pressure conversion factor                |
| COND   | X               | Condensate mass fraction in g/kg           |
| CPØ    | $C_p$           | Specific heat                              |
| CUS    | $C_g$           | *Under-saturated equilibrium concentration |
| CVØ    | $C_v$           | Specific heat                              |
| CLINF  | $C_{ls}$        | Saturated equil. $C_g$                     |
| ClØ    |                 | $C_l$ (frozen equil., see Appendix 2)      |
| Cl     | $C_l$           | *Equil. monomer conc.                      |
| ClØ    | $C_l$ (initial) | *Initial monomer conc.                     |
| Cl1    | $C_{l1}$        | *Eq. 8.2, Ref (1)                          |
| Cl2    | $C_{l2}$        | *Eq. 8.4, Ref (1)                          |
| ClG    | $C_{lg}$        | *Eq. 8.4, Ref (1)                          |
| ClKE   |                 | *Eq. III-8.7, 2nd term                     |
| C2KE   |                 | *Eq. III-8.7, 3rd term                     |
| CGKE   |                 | *Eq. III-8.7, 4th term                     |
| CGVIB  |                 | *Eq. III-8.7, 5th term                     |
| CGWK   |                 | *Eq. III-8.8, 6th term                     |
| DADX   | $dA/dx$         | Slope, nozzle area                         |
| DADXMG |                 | Sub-interval $dA/dx$                       |
| DAMG   |                 | Sub-interval $dA$                          |
| DDADX  | $d(Dadx)$       |  |

|        |                     |   |
|--------|---------------------|---|
| DDU    | $d^2u$              |   |
| DELEP  | $\Delta \epsilon_g$ | See Eq. V-1.4   |
| DELEPØ | $\Delta c^\circ_g$  | Eq. V-1.2   |
| DELTAP |                     | $P_{\text{static}} - P_{\text{isentropic}}$             |
| DELTAT |                     | $T_{\text{static}} - T_{\text{isentropic}}$<br>reaction |
| DELTAX |                     | Experimental data<br>interval                           |
| DELZI  | $\Delta \xi$        | $\xi_g - \xi_{g-1}$                                     |
| DELZET | "                   | * "   |
| DENOM  |                     | Denominator, Eq.<br>V-2.7                               |
| DENOM1 |                     | First term, DENOM                                       |
| DENOM2 |                     | Second term, DENOM                                      |
| DENIS  |                     | DENOM, no reaction<br>(isentropic case)                 |
| DFG    | $df_g$              | Eq. V-1.13 (total)                                      |
| DFGA   | $df_g$              | Eq. V-1.12 (reaction)                                   |
| DFGEX  |                     | Eq. V-2.11 (expansion)                                  |
| DFGM1  | $df_{g-1}$          | Eq. V-1.13  |
| DFGP1  | $df_{g+1}$          | Eq. V-1.13  |
| DFØ    | $df_o$              | Eq. V-2.12  |
| DF1ØD  | $df_1$ Initial      | Initial value, no<br>reaction                           |
| DFG12  | $df_1$              | Eq. V-2.15  |
| DFG1EX | $df_1$              | Eq. V-2.11  |
| DFG2   | $df_2$              | Eq. V-2.13, $g=2$                                       |

|        |          |  |
|--------|----------|--|
| DFG2M1 |          | DFG2, previous time increment              |
| DLDG   | $m_A$    | Eq. III-4.1                                |
| DPISEN | $dp_i$   | Eq. V-2.10, no reaction                    |
| DPSTAT | $dp$     | Eq. V-2.10 or V-2.9                        |
| DQ     | $dq$     | $(dq/dt)dt$                                |
| DQDT   | $dq/dt$  | Eq VIII-3                                  |
| DQDX   | $dq/dx$  | $(dq/dt)/u$                                |
| DTISEN | $dt_i$   | Eq. V-2.7, no reaction term                |
| DTM    | $dt$     | in seconds                                 |
| DTSTAT | $dT$     | Eq. V-2.7                                  |
| DU     | $du$     | Experimental velocity increment            |
| DUDXMG |          | $du$ , calculating                         |
| DXCM   | $dx$     | Increment of length along nozzle axis      |
| D1     |          | Eq. VIII-3                                 |
| D2     |          | "  |
| D3     |          | "  |
| EPSIF  |          | *Iteration limit, statement 240            |
| ETAG   | $\eta_g$ | Eq. III-8.2                                |
| FGTM   | $f_g$    | Non-stationary concentration ( $cm^{-3}$ ) |
| FI     |          | *Eq. (8.8)+1, Ref (1), 3rd term            |
| FIRST  |          | Eq. VI-2.1, 1st term                       |
| FIRST  |          | *Eq. III-8.7, 1st term                     |

|        |                          |   |
|--------|--------------------------|---|
| FØTM   | $f_0$                    | Carrier gas concentration ( $\text{cm}^{-3}$ )          |
| FØTMØ  |                          | $f_0$ , initial   |
| FTHETA | $F(\theta)$              | *Prom Eq. 8.6, Ref (1)                                  |
| FRT    | $F(\theta)$              | *Eq. 8.15, Ref (1)                                      |
| FTHETG | $F(g, \theta)$           | *Eq. 8.6, Ref (1)                                       |
| F1ØD   |                          | $f_1$ , no reaction, initial                            |
| F1TM   | $f_1$                    | Non-stationary monomer concentration                    |
| F1TMØ  |                          | $f_1$ , initial   |
| F1C1R  |                          | $f_1/C_{1s}$ , same temp. Eq. VI-2.1                    |
| FITERM |                          | Eq. V-2.7, 2nd term                                     |
| F2TM   | $f_2$                    | Non-stationary dimer concentration ( $\text{cm}^{-3}$ ) |
| GAMA   | $\gamma$                 | Numerical constant, see App 3                           |
| GAMAS  | $\Gamma$                 | Surface tension, dyne/cm                                |
| GAMAD  | $\gamma_d$               | $(u_{00}^0/u_{11}^0)^{1/2}$ for dimer                   |
| GBAR   | $\bar{g}$                | Average cluster size                                    |
| GGPIG  | $X$                      | Eq. V-2.12  |
| GLMDA  | $\lambda_g$              | Coordination number                                     |
| GMAX   |                          | * = MAXG, below   |
| GINF   | $g_\infty$               | numerical infinity for cluster size                     |
| GRATIO | $G(\theta)/G(g, \theta)$ | * $>L_g/L_\infty$ , pg 1282, Ref 1.                     |

|        |                |  |
|--------|----------------|--|
| GTHETA | $G(g, \theta)$ | *Eq. 8.9, Ref 1                                      |
| LG     | $g-1$          |  |
| M      | $g+1$          |  |
| MAXG   |                | Upper limit on actual calculation                    |
| MAXGPI |                | MAXG plus 1  |
| MG     |                | Subinterval index                                    |
| NG     |                | Calculating limit                                    |
| NGAMA  |                | Experimental interval divisor                        |
| NSTEP  |                | Stepping index                                       |
| NØ     |                | Index locating start of calculation                  |
| PAIR   |                | Initial partial of an Isentropic pressure, cm Hg     |
| PCOEF  |                | Conversion factor                                    |
| PI     | 3.14159        |  |
| PINF   | $P_s$          | Equilibrium saturation vapor pressure                |
| PISEN  | $P_i$          | Isentropic static pressure (no reaction)             |
| PPAR   | $P_v$          | Partial pressure of vapor                            |
| PPARØ  |                | $(p_v) = \text{initial}$                             |
| PRES   |                | *Calc. pressure, cm. Hg.                             |
| PSTAT  | $p$            | Static pressure of carrier gas vapor                 |
| PVAP   |                | Partial pressure at initiation of program, ref. only |

|        |                |   |
|--------|----------------|---|
| PØ1    |                | Static pressure<br>at inlet conditions  |
| QOFX   | $Q(x)$         | $\sum_x dq$ , See DQ                    |
| RDTM   | dt             | Time increment<br>(corrected)           |
| REF    |                | Eq. V-2.15                              |
| RMATG2 | $df_g/dt$      | Eq. V-1.12                              |
| RMATØ  |                | Eq. V-2.12                              |
| RMAT22 |                | Eq. V-1.12, g=2                         |
| RMAT1Ø |                | Eq. V-2.11, F,<br>isentropic            |
| EMI'FJ | $R_g^-$        | Table V-1.1                             |
| RMIUF1 | $R_{g+1}^-$    | Table V-1.1                             |
| RMI2BI | $R_2^-$        | Table V-1.1                             |
| RMI3U  | $R_3^-$        | Table V-1.1                             |
| RMI4U  | $k_4^-$        | Table V-1.1                             |
| RPLUS  | $R_g^+$        | Table V-1.1                             |
| RPLGP1 | $R_{g+1}^+$    | Table V-1.1                             |
| RTAA   |                | Eq. V-2.5 (see<br>comment in program)   |
| RTUU   |                | Eq. V-2.5 (See<br>comment in program)   |
| RØ     | $r_o$          | Mean molecular radius<br>carrier gas    |
| RI     | $r_1$          | Mean molecular radius<br>vapor          |
| S      | s              | Saturation ratio                        |
| SIGMAL | $\sigma_{1,g}$ | Eq. III-1.5, collision<br>cross section |



|        |                   |  |
|--------|-------------------|--|
| SIGØ1  | $\sigma_{0,1}$    | Collision cross-section, carrier gas - monomer     |
| SIGØ2  | $\sigma_{0,2}$    | Collision cross-section, carrier gas - dimer       |
| SIG11  | $\sigma_{1,1}$    | Collision cross-section, monomer-monomer           |
| SIG12  | $\sigma_{1,2}$    | Collision cross-section, monomer - dimer           |
| SIGIG  | $\sigma_{1,g}$    | *See SIGMA   |
| SIG1G1 | $\sigma_{1, g-1}$ | *See SIGMA   |
| SIG1Ø1 | $\sigma_{1,01}$   | Collision cross section, mixed pair <sup>(1)</sup> |
| SLDADX | $d^2A/dx^2$       | Slope of DADX                                      |
| SLDU   | $d^2u$            |  |
| SLU    | $du$              |  |
| SLUM   |                   | $du$ at $x-1$                                      |
| SMGDFG | $\Sigma gdf_g$    | Alternate expression for Eq. V-1.5                 |
| SMNGRG |                   | Eq. V-1.6, 1st term                                |
| SRDTM  | $t$               | $\Sigma dt$  |
| SUM    | $\log \bar{v}$    | Eq. VI-2.1   |
| SUMCHI | $\Sigma X_g C_g$  | See Eq. III-8.7                                    |
| SUMCG  | $\Sigma C_g$      | " " "  |
| SUMCGG | $\Sigma g C_g$    | Eq. 8.17, Ref (1)                                  |
| SUHDAX | $\Sigma A (DADX)$ | See App 3, multipoint derivatives                  |

|        |                                     |   |
|--------|-------------------------------------|---|
| SUMDDU | $\Sigma \Delta (DU)$                | See App 3, multi-point derivatives              |
| SUMDU  | 2DU                                 | "   |
| SUMBRC |                                     | Eq. V-1.8, $\Sigma \{ \}$                       |
| SUMGFG | $\Sigma f_g$                        |   |
| SUMGG  | $\Sigma g f_g$                      |   |
| SUMLCG |                                     | See 1st term, Eq. III-8.7                       |
| SUMLNW | $\Sigma (\omega_i / \omega_\infty)$ | See eq. 8.13, Ref (1)                           |
| SXER   | d/dx (XER)                          | Appendix VIII-4                                 |
| TDK    | T                                   | Temperature °K                                  |
| TDKIS  | $T_i$                               | Temperature, isentropic °K                      |
| TDKØ   | $T_0$                               | Temperature at initiation of calculations       |
| TDKØØ  | $T_{00}$                            | Temperature at inlet conditions                 |
| THETA  | $\theta$                            | $\theta = u^\circ_{11} / kT$                    |
| U      | u                                   | Flow velocity                                   |
| UFAC   |                                     | $u^\circ_{11} = UFAC \times u^\circ_{11}$       |
| UMG    |                                     | Flow velocity, sub-interval                     |
| WG     | $\omega_g$                          | Eq. 8.3, Ref 1                                  |
| WG3    | $\omega_3$                          | " for g=3                                       |
| WINF   | $\omega_\infty$                     | " for g= $\infty$                               |
| UØØØ   | $u^\circ_{00}$                      | Pair interaction energy carrier gas-carrier gas |

|             |                                |   |
|-------------|--------------------------------|---|
| U $\phi$ 01 | u $^{\circ}$ 01                | Pair interaction energy carrier gas - monomer |
| U $\phi$ 11 | u $^*$ 11                      | Pair interaction energy monomer - monomer     |
| XCM         |                                | distance on nozzle centerline                 |
| XER         |                                | multiplier, see program                       |
| XER $\phi$  |                                | Initial XER                                   |
| XJ          |                                | Computer index (note XJ)                      |
| XKG         | $\kappa_g$                     | *Eq. 8.5, Ref (1)                             |
| XKGL1       | $\kappa_{g-1}$                 | "   |
| XK2         | $\kappa_2$                     | "   |
| XLD1F       | $\lambda_{\infty} - \lambda_g$ | * $\bar{v} > 0$                               |
| XLEGC1      |                                | *See eq. 8.10, Ref (1)                        |
| XLG         | $L_g$                          | *Eq. 8.9, Ref (1)                             |
| XLGTDK      |                                | Eq. V-2.14                                    |
| XLHT        | L                              | *Eq. III-8.7                                  |
| XLOGCG      |                                | *See eq. 8.10, Ref (1)                        |
| XLOGC1      |                                | *See eq. 8.10, Ref (1)                        |
| XLOGC       |                                | " "   |
| XLOGNU      | $\log \bar{v}$                 | Eq. V-2.14                                    |
| XLPINF      | $\log p_{\infty}$              | Eq. IV-1.2                                    |
| XLRTIO      | $L_g/L_{\infty}$               | *Pg. 1282, Ref (1)                            |

|         |               |  |
|---------|---------------|--|
| XMABAL  | $X_1$         | Specific humidity                          |
| XMØ     | $m_o$         | Molecular mass,<br>carrier gas             |
| XM1     | $m_1$         | Molecular mass,<br>vapor                   |
| XMUØ    | $\mu_{o,g}$   | Reduced mass,<br>carrier gas - cluster     |
| XMU1    | $\mu_{1,g}$   | Reduced mass,<br>monomer - cluster         |
| XMU1G   | $\mu_{1,g}$   | "  |
| XMU1G1  | $\mu_{1,g-i}$ | "  |
| XMU12   | $\mu_{1,2}$   | Reduced mass,<br>monomer - dimer           |
| XMUØ2   | $\mu_{o,2}$   | Reduced mass,<br>carrier gas - dimer       |
| XNOWDA  | NONDAT        | Input data file                            |
| XNOW2   | NON2          | Input data file                            |
| XNU     | $\bar{v}$     | Circulation frequency                      |
| XNUMBER |               | Eq. V-2.7, numerator                       |
| XNUM1   |               | Eq. V-2.7, 1st & 2nd<br>terms of numerator |
| XNUM2   |               | Eq. V-2.7, 3rd term<br>of numerator        |
| XNUMIS  |               | Eq. V-2.7, no<br>reaction                  |
| XOUTFI  |               | Output file                                |
| ZETAG   | $\zeta_g$     | *Eq. 8.13, Ref (1)                         |
| ZI1     | $\xi_1$       | Monomer rotational<br>mode                 |
| ZIGDD   | $Z_{1,g}^*$   | Eq. V-2.11,<br>collision number            |

|        |               |            |
|--------|---------------|------------|
| Z1M1DD | $Z_{1,g-1}^n$ | Eq. V-2.11 |
| ZØ1DD  | $Z_{0,1}^n$   | Eq. V-2.11 |
| ZØ2DD  | $Z_{0,2}^n$   | Eq. V-2.11 |
| Z11DD  | $Z_{1,1}^n$   | Eq. V-2.11 |
| Z12DD  | $Z_{1,2}^n$   | Eq. V-2.11 |
| ZØ11DD | $Z_{1,01}^n$  | Eq. V-2.11 |

## APPENDIX 2

### FORTRAN PROGRAM FOR CLUSTER DISTRIBUTIONS AT SATURATED EQUILIBRIUM

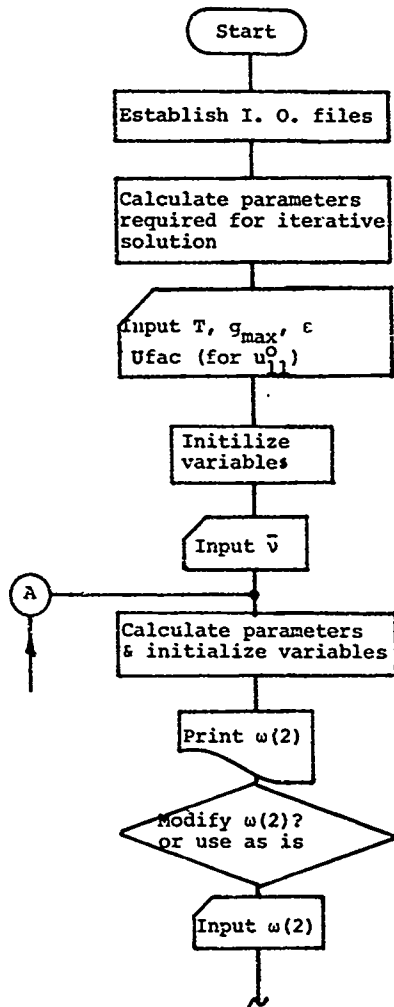
The solution given is for water vapor in air but it can be applied to any mixture of a vapor and a carrier gas. Inputs required are:  $T$ ,  $g_{\infty}$ ,  $\epsilon$ ,  $g_{\max}$ ,  $r_1$ ,  $r_0$ ,  $u_{11}^0$ ,  $m_1$ ,  $m_0$ ,  $\sigma_{11}$ ,  $P_v$ ,  $C_1$ ,  $\lambda_{\infty}$  and  $m_i$ , the nomenclature used being given in Appendix 1. The iteration involved is given in Table III-2.1 and Flow Chart VIII-2.1.

A term in the program but not yet described is UFAC. This is a multiplier which facilitates the alteration of  $u_{11}^0$  from the value of  $u_{11}^0 = 1500K$  (erg/°K) (or 2.98 K cal/mole assumed initially).

A further remark concerns  $\sigma_{11}$ . According to the cluster theory<sup>(1)</sup>, hard sphere collision diameters are to be used. The value used here, however, is not  $\sigma_{11} = 2.00r_1$  but rather  $\sigma_{11} = 2.05r_1$ . This value was obtained by cross iteration between the present equilibrium solution and the non-equilibrium solution of Appendix 3. The value of  $\sigma_{11}$  was adjusted until the cluster reaction rates became stationary to about 5 digits when the equilibrium distribution of cluster sizes was fed into the non-equilibrium program. Vapor pressure data<sup>(5)</sup> for liquid water when fitted by least squares approximation yields  $p_{\infty} = 9.3286 - 2367./T$  while the expression for adiabatic expansion of moist air from an initial temperature of 295°K and specific humidity of about 5g/kg is  $P = 0.425 (T/273)^{3.5}$ . The pressure conversion factor cm Hg to dynes/cm<sup>2</sup> is  $1.33 \times 10^3$ .

Once initial conditions have been selected, the iteration in Table III-2.1 may proceed with the objective of satisfying limiting constraints (1) through (5); condition (6) is dealt with later in Appendix 3. For each cluster size from  $g = 2$  upwards to an arbitrary upper limit  $g_{\max} < g_{\infty}$  equation III-5.1 must be solved for the concentration  $C_g$  ( $\text{cm}^{-3}$ ). Also calculated is  $\zeta_g$ . The approach of  $\Delta\zeta$  to zero as  $g$  approaches numerical infinity can be checked numerically in file F2 or plotted separately for inspection.

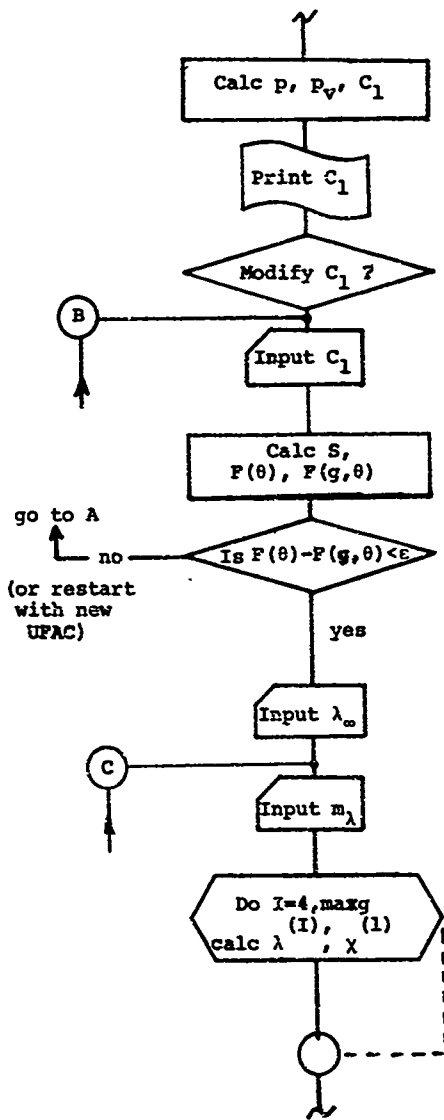
To calculate a super or undersaturated cluster distribution one must first calculate the saturated distribution at the same temperature to obtain the value of  $C_1$  in statement 915 for CLINF. Statement 800,  $P = P_v$  must be deleted and statement 1010 deleted. All other parameters remain the same as for the saturated solution at that temperature.

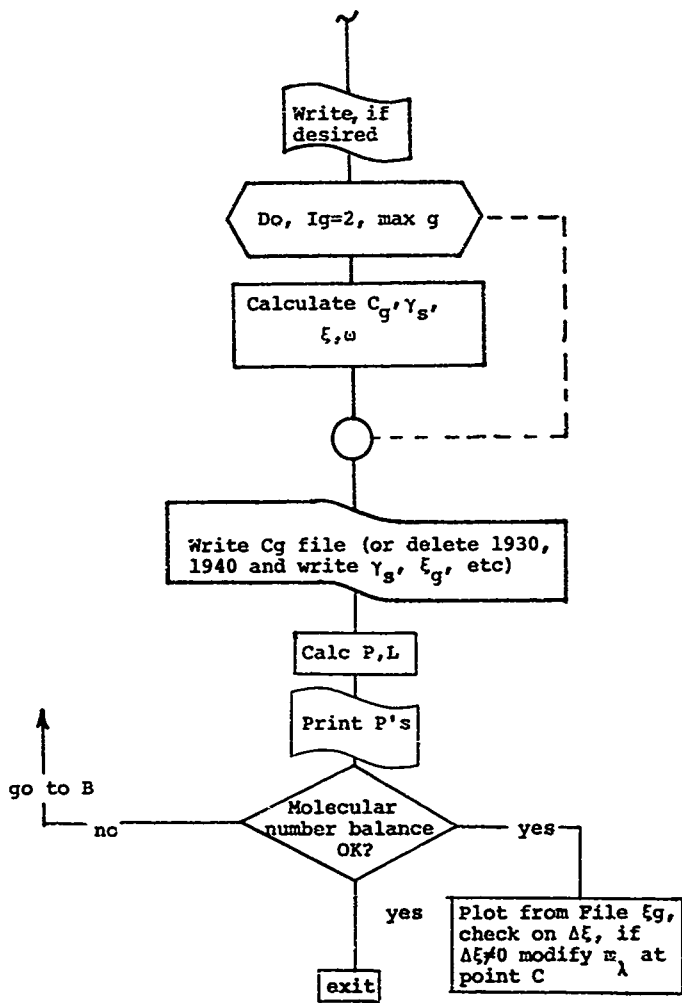


Flow Chart for Computation of Stationary Distributions

Figure VIII-2.1







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40 01

```
110 DIMENSION C(300),GLADA(300),BIGG(300),CUS(300),I9(300)
120 DIMENSION ZEFAG(300),XLJGC1(300),GALAS(300),DELZET(300)
130 DIMENSION GRAT(300),XLRAT(300),CHI(300)
140C- PROBLEM NAME IS H0.40
160C- CLUSTER DISTRIBUTIONS AT EQUILIBRIUM
170 FILENAME F2
180 F2="H0R2"
190 FILENAME F3
200 F3="H0R3"
210 FILENAME I1
220 IN=" "
230 FILENAME OUT
240 OUT=" "
250 WRITE(OUT,150)
260 WRITE (OUT,90000)
270 INPUT,TDK
280 WRITE(OUT,200)
290 WRITE (OUT,90000)
300 INPUT,GMAX
310 WRITE (OUT,201)
320 WRITE (OUT,90000)
330 INPUT,EPSIF
340 GLADA1=6.0
350 BK=1.38E-16
360 NAX=1
370 PI=3.14159
380 NAXG=GMAX
390 R1=1.4E-08
400 AG(1)=1.0
410 UO11=1500.0*BK
420 WRITE (OUT,202)
430 WRITE (OUT,90000)
440 INPUT,JFAC
450 J011=UO11*JFAC
460 UO00=UO00*JFAC
470 UO01=SQRT(UO11*UO00)
480 THETA=UO11/(BK*TDK)
490 GLADA(1)=0.0
510 GLADA(2)=1.0
520 GLADA(3)=2.0
530 BIGG(1)=0.0
540 BIGG(2)=1.0
550 BIGG(3)=2.0*(EXP (THETA)-1.0)/(1.0+2.0*THETA)
552 CHI(2)=1.0
553 CHI(3)=3.0
560 X11=3.04E-23
570 X12=4.93E-23
580 X1312=2.04E-23
590 WRITE (OUT,230)
600 WRITE (OUT,90000)
```

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19.001 (continues)

```

610      LIPU1,XHUBAR
612      TDKO=2/3.0
613      LOGU=ALOG(XHUBAR)/2.30258
614      XLGDKX=LOGU-TDKO/TDKO
620      SIG11=2.0**X1
625      SIG12=1.95**X1
630      Z11=X-3.33E-13**SORT(TDK/XM1)*SIG11**2
635      Z11=X-Z11**2/2.0
640      C11=Z11**2**SORT(THETA)
650      RG(2)=C11*EXP(THETA)/(XHUBAR**SORT(THETA))
655      RG(2)=Z11**2**EXP(THETA)/XHUBAR
670      221      ..ITE(OUT,232)
680      ..ITE(OUT,234)RG(2)
690C-      PIF HERE IS FOR LIQUID
700      HRTIE(OUT,235)
710      DRIFE(OUT,90000)
720      LIPU1,RG(2)
730      222      XLP1=X-3.33E-13*(1/3/TDK)
740      P1=X-10.0**X(XLP1**2)
750C-      P1 IS THE SATURATION VAPOR PRESSURE IN CM HG
760C-      P IS ISENIOPIC PRESSURE IN CM HG
770      P=0.4525*(TDK/273.0)**3.5
780      EXP=1.33E+03
790      PV=P*H/10.0
800      P=PIF
810      PIF HERE IS SAT. PRES. IN DYNES/CM**2
820      P1,P=EXP*PIF
830      C1=0.9**X+10**X/TDK
840      C10=C1
850      223      ..ITE(OUT,237)
860      ..ITE(OUT,239)C1
870      ..ITE(OUT,239)
880      ..ITE(OUT,239)
890      LIPU1,C1
900      P=P/P1
910      LIPU1=0.11/(PIF*THETA)
915      C11=LIPU1
920      LIPU1=1.0/C11**2
930C-      THETA NOW REFERS TO ASYM. VALUE
940      ALIPU1=(1.0/(36.0*PI))**0.333
950      HIGU=5.0**X1**2**SORT(UO11/XM1)/XHUBAR
960      FRI=PIF/(CIG**XLINF)
970      240      FRI=(EXP(GLADAI*THETA)-1.0)/(SORT(THETA)*
980      *(1.0+GLADAI*THETA+0.5*(GLADAI*THETA)**2))
990      DELU=ASIN(FTHETA-FRI)
1000      ..ITE(OUT,238) FTHETA,FRI,DELF
1010      IP(DELU-DELF)260,260,245
1020      241      ..ITE(OUT,239)
1030      ..ITE(OUT,239)
1040      LIPU1,GLADAI

```

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10201 (continued)

```

1050      GO TO 240
1060 200 WRITE (OUT,992) FTH-ETL,FRT,DELF
1062      GL-LIQ=3.04
1065      XLATEI=UFAC*2.98*GLMDAI
1066      PRINT,XLATEI
1070      XJ=ALOG(C1*JL,IF)
1080      INF=122
1090      GINF=INF
1092      WRITE(OUT,210)
1094      WRITE(OUT,99099)
1096      INPUT,DLDG
1100      DELLD=GLMDAI-GLMDA(3)
1110      DG 280 I=4, 4AXG
1120      I=I
1130      L=L-1
1140      IF(I-INF)255,275,275
1150 205 GLMDA(I)=GLMDA(L)+DLDG
1152      CHI(I)=CHI(L)+3.0
1160      GO TO 230
1170 275 GLMDA(I)=GLMDA(L)
1172      CHI(I)=CHI(L)+3.0
1180 230 CONTINUE
1185 290 CONTINUE
1200      SJSCG=0.0
1210      SJACG=0.0
1220      SUALCG=0.0
1230      SJAUM=0.0
1240      C(I)=C1
1250      GTHETA=FTHETA*SURT(THETA)/EXP(THETA)
1260      E-J=EXP(-J)
1270      GO TO 400
1280 300 WRITE(OUT,310)
1290      WRITE(OUT,311)S,C1,PV
1300      WRITE(OUT,312)XJ,THETA,GLMDAI
1310      WRITE(OUT,313) SIGM,GINF,GANAS
1320      WRITE(OUT,314) GMAX,XHUBAR,XNUO1
1330      WRITE(OUT,315)UO11,UO01,UO00
1340      WRITE(OUT,99996) E-J
1350 400 (A 09) IG=2,4AXG
1360      U=U
1370      LU=IG-1
1380      SLL=U-1.0
1390      SIGIG=PI*(1.0+G**0.333)
1400      XJIG=XJ*(G/(1.0+G))
1410      IF(IG=20)410,410,415
1420 410 ALPHAG=1.0
1430      GO TO 420
1440 415 ALPHAG=1.0-0.1*(G/GINF)
1450 420 CONTINUE
1460      XKG=(SIGIG/RI)**2/SORT(XJUIG/XMI)

```

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1600 (continued)

```

1670      IR(IG-2)999,495,453
1680      43) COEFFI JE
1690      IR(IG-3)999,400,450
1700      45) COEFFI JE
1710      THETA(IG)=(EXP(THETA*(GLADA(IG)-1.0))
1720      &-(EXP(THETA*(GLADA(IG)-GLADA(LG)-1.0)))/
1730      &(1.0+GLADA(IG)*THETA+.5*(GLADA(IG)*THETA)**2)
1740      A=3.0*-7.0
1750      FI=3.0*A*(A-1.0)/((A-2.0)*(A-3.0)*(A-4.0))
1760      SIG1=PI*(1.0+GL1**0.333)
1770      XAL1=X AL*(GL1/(1.0+GL1))
1780      XGL1=(SIG1/PI)**2/SQRT(XMU1G1/X AL)
1790      XLG=(XGL1/ALPHA)*FI
1800      FTHETA=(EXP(THETA)/SQRT(THETA))*BIGG(IG)
1600      IR(IG-4)999,455,470
1610      45b) FTHETA=FTHETA*(1.0/3.0)
1620      GO TO 470
1630      460) FTHETA=(EXP(THETA)/SQRT(THETA))*BIGG(IG)
1640      ZP2=.99E-09*SQRT(TDK)
1650      XAL12=X AL*(GL1/(1.0+GL1))
1660      C12=(ZP2*(SIG12)**2/SQRT(XMU12))*SQRT(THETA)
1670      SIG(IG)=C12*FTHETA/XAL12
1680      XAL2=(SIG12/PI)**2/SQRT(XMU12/X AL)
1690      XG3=BIGG*XAL2*FTHETA
1700      470) IG 495
1710      ZP2=.99E-09*SQRT(TDK)
1720      C12=(ZP2*(SIG12)**2/SQRT(XMU12))*SQRT(THETA)
1730      SIG(IG)=C12*FTHETA/XAL12
1740      XAL2=XAL2*(XAL12/XAL1)
1750      XG3=XG3*(XAL12/XAL1)
1760      495) SJALN=SQRLN+ALOG(SIG(IG)/41NF)
1770      FLST=(G-1.0)*XJ
1780      ZETAG(IG)=-3K*TDK*SUXLN
1790      XAL5(IG)=10.2216F14*(ZETAG(IG)/G)
1800      XLOGC1=XJ*(G-1.0)+SUMLN
1810      XLOGC1(IG)=XLOGC1/2.30258
1820      XLOGC2=XLOGC1(IG)+ALOG(C1)/2.30258
1830      C(IG)=1.0**XLOGC2
1840      ZTAG=GL1
1850      EFAO=GLADA(IG)/2.
1860      SLC=(X*GL1*(IG-ETAG)*C(IG)
1870      SJALC=SIG*SLC+SLC
1880      SJALC=SIG*SLC+C(IG)
1890      SJALC=SUMGC+G*C(IG)
1900      SJALC=SUMCHI+CHI(IG)*C(IG)
1910      XLRTIO=XLG/XLINF
1920      GRATIO=THETA/BIGG(IG)
1930      XLRTIF=GLADA1-GLADA(IG)
1940      GRATIO(IG)=GRATIO
1950      XLRTIO(IG)=XLRTIO
1960      DELZ=FI(IG)=ZETAG(IG)-ZETAG(IG-1)

```

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00801 (continue)

```

1920 090 CONTINUE
1930 WRITE(F2,2121)(IG,C(IG),IG=1,MAXG)
1940 GO TO 840
1950 695 WRITE(F2,2120)(IG,GAMAS(IG),ZETAG(IG),NG(IG),GRAT(IG),XLRAT(IG)
1960 ,IG=1,MAXG)
1970 597 CONTINUE
1980 WRITE(F3,2121)(IG,XLOGC1(IG),IG=1,MAXG)
1990 GO TO 840
2000 700 WRITE(OUT,811)
2010 IF(LAP-2)320,330,830
2020 120 WRITE(OUT,812)(IG,C(IG),XLOGC1(IG),NG(IG),ZETAG(IG),IG=1,
2030 ,MAXG)
2040 GO TO 840
2050 330 WRITE(OUT,812)(CUS(IG),GLADA(IG),BIGG(IG),IG=1,MAXG)
2060 340 CONTINUE
2070 R11=SUJCG+C1
2080 R12=SUJCG-C(2)
2090 R13=JLALIO*C1+SUJLCC
2100 900 CF=7.0E-05
2110 UBR=.30+(1.0/200.0)*(273.-TDK)
2120 PRES=(U011/DHEIA)*R11*CF
2130 C1KE=(6./2.)*(3.2965E-24/XM1)*TDK*C1/C10
2140 C2KE=(5./2.)*(3.2965E-24/XM1)*TDK*(2)/C10
2150 C3KE=3.0*(3.2965E-24/XM1)*TDK*R12/C10
2160 CGV1=(3.2965E-24/XM1)*TDK*SUJCHI/C10
2170 CGK1=(3.2965E-24/XM1)*TDK*R11/C10
2180 FIRST=(2.383E-08*U011/XM1)*(R13/C10)
2190 XLH=FIRST+C1KE+C2KE+CGKE+CGV1+CGK1
2200 PISEN=P
2210 PRINT,FIRST,C1KE
2220 PRINT,C2KE,CGKE
2230 PRINT,CGV1,CGK1
2240 900 WRITE(OUT,317)PISEN,PV,PRES
2250 WRITE(OUT,320)GAMAS(123)
2260 WRITE(OUT,330)XLH
2270 910 GO TO 225
2280 999 STOP
2290 90000 FORMAT(2H ?)
2300 100 FORMAT(29H TYPE IN INITIAL VALUE OF TDK)
2310 200 FORMAT(13H TYPE IN GMAX)
2320 201 FORMAT(14H TYPE IN EPSIF)
2330 202 FORMAT(13H TYPE IN UFAC)
2340 210 FORMAT(13H TYPE IN DLDG)
2350 230 FORMAT(24H TYPE IN VALUE OF XNUBAR)
2360 232 FORMAT(17H CALCULATED NG(2))
2370 234 FORMAT(7H NG(2)=E15.5)
2380 235 FORMAT(14H TYPE IN NG(2))
2390 237 FORMAT(14H CALCULATED C1)
2400 239 FORMAT(11H TYPE IN C1)
2410 238 FORMAT(4H C1=E15.6)

```

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2310 311 POLY A(10)0 PV=E10.3  
 2320 31 POLY A(10)0 KJ=E10.3,10H HETA=E10.5,  
 2330 101 SLASAI=E10.3)  
 2340 315 POLY A(10)0 SIG=E10.3,10.1 HIF=E10.3,  
 2350 101 GAS=E10.3)  
 2360 31 POLY A(10)0 GMAX=E10.5,10H SUBAR=E10.3,  
 2370 101 G001=E10.3)  
 2380 315 POLY A(10)0 G011=E10.3,10H G001=E10.3,  
 2390 101 G000=E10.3)  
 2400 315 POLY A(10)0100IG(IG)=E10.3,10H GR=E10.3,  
 2410 101 DELGR=E10.3)  
 2420 31 POLY A(10)0 PRR=E10.3,10H IG(IG)=E10.3,  
 2430 101 HETA=E10.3)  
 2440 317 POLY A(10)0 PISEN=E10.3,7H PV=E13.6,  
 2450 101 PIES=E13.6)  
 2460 320 POLY A(12)1 GAS(123)=E13.6)  
 2470 330 POLY A(10)1 HIF=E13.6)  
 2480 101 POLY A(10)1,5)  
 2490 311 POLY A(31)0 CONCENTRATIONS, G=1 TO GMAX)  
 2500 12 POLY A(2X,10,2X,E10.3,3X,E10.3,3X,E10.3,3X,E10.3)  
 2510 211 POLY A(E10.3)  
 2520 2121 POLY A(10,20,E15.6)  
 2530 212 POLY A(E10.3)  
 2540 18 POLY A(11),50,3E10.5)  
 2550 2120 POLY A(10,21,E15.6,2H,E15.6,2H,E15.6,  
 2560 21,E15.6)  
 2570 2130 POLY A(10,2H,E15.6,2H,E15.6,2H,  
 2580 20 POLY A(3E10.5)  
 2590 2090 POLY A(E10.5)  
 2600 2090 POLY A(1X,3E10.5)  
 2610 2090 POLY A(1X,2E10.5)  
 2620 2090 POLY A(1X,E10.5)  
 2630 2090 POLY A(1X,10,3E10.5)  
 2640 2090



### APPENDIX 3

#### FORTRAN PROGRAM FOR NON-EQUILIBRIUM CLUSTER DISTRIBUTION DURING AN ADIABATIC EXPANSION

The calculation given here is for the expansion of water vapor in air in a supersonic nozzle of known geometric profile. Solution of the one dimensional equations of motion <sup>(7,8)</sup> yields the flow velocity  $u$  which is required as an input datum. The same solution gives the cross sectional area  $A$  and its rate of change along the flow axis  $dA/dx$ . Also required are the initial equilibrium cluster distribution from Appendix 2 and the cluster properties such as radius  $r$ , pair interaction energy  $u_{11}^0$ .

The computational scheme or flow chart is given in Figure VIII-3.1 and the relation of the iteration time interval to data increments given in Figure VIII-3.2. The method is to divide the data interval ( $\Delta x = 1$  mm) into sub intervals ( $\Delta x/\gamma$ ) small enough to allow a non-oscillating solution by Eulerian numerical integration:

$$f(x + \Delta x/\gamma) = f(x) + d f/dx(\Delta x/\gamma) \quad \text{VIII-3.1}$$

However, the fewer the subdivisions the shorter the computation time. The smallest value of  $\gamma$  giving stability was found to be about 5000 and this value already brings the calculation interval down to the order of the molecular collision time. An extensive effort was necessary to find a method to reduce the amount of computer time involved. Additional complications in that the collision time increases during the expansion process

and the numerical interval in Equation VIII-3.1 must be significantly longer than the collision interval to be consistent with equilibration of translational energies. An approximation technique yielding stable numerical results was developed after many trials. After dividing a data interval:  $\Delta x' = \Delta x / \gamma$ , with a value of  $\gamma$  around 5000, a multiplier, XER for example, XER=2.0 is selected arbitrarily. This multiplier has the effect of lengthening the calculation interval because the second term in Equation VIII-3.1 becomes

$$\Delta x / \gamma \quad (XER) \quad d F / dx \quad \text{VIII-3.2}$$

To reduce the number of calculation intervals within the original data interval  $\Delta x$ , an end condition NSTOP is introduced where  $NSTOP = \gamma / XER$ . If XER is 2.0, the derivative  $d F / dx$  is thus applied over a length  $\frac{2\Delta x}{\gamma}$  for each  $\gamma$  interval, but the calculation for a given data interval is terminated after  $\gamma / 2$  sub intervals. To take account of the increase in collision time due to expansion, the collision time for the  $g = 10$  cluster is calculated at the beginning and end point of the overall calculation (an increase from about .5 nsec to 4nsec) and a linear fit to XER is determined. An increment SXER is added to XER and NSTOP recalculated before calculating over the next data interval. Thus, a crude correspondence between the collision interval and the calculation interval is maintained and the amount of computer time is reduced since NSTOP is decreasing continually.

In as much as the calculation proceeds at near the molecular

collision interval, interpolation of the experimental input data and the calculated flow velocity  $u$  is required. Multi-point (seven) derivatives are taken over the original numerical data and velocity then applied each  $\gamma$  subinterval. Thus, the original data for nozzle slope,  $DADX(J)$  (INDEX J increments each m.m.) becomes  $DADKNG$  for each  $\gamma$  interval. The expansion terms, Equation V-2.11 and V-2.12 are then corrected each  $\gamma$  interval.

Additionally, after calculating all rates up through  $g_{\max}$  at any subinterval, the rates for cluster size ( $g_{\max}+1$ ) must be calculated to include the influence of  $f_{g+1}$  on  $f_g$ . In this calculation the influence of  $g_{\max} + 2$  is ignored so that

$$\frac{df_{g_{\max}+1}}{dt} = (R_{g+1}^+ - R_{g+1}^-) - f_{g+1} \frac{d}{dt} (\ln v)$$

rather than Equation V-2.13. This result is correct within a few percent as long as  $f_{g+2} \ll f_{g+1}$ . The calculation appears after statement 525 in the program.

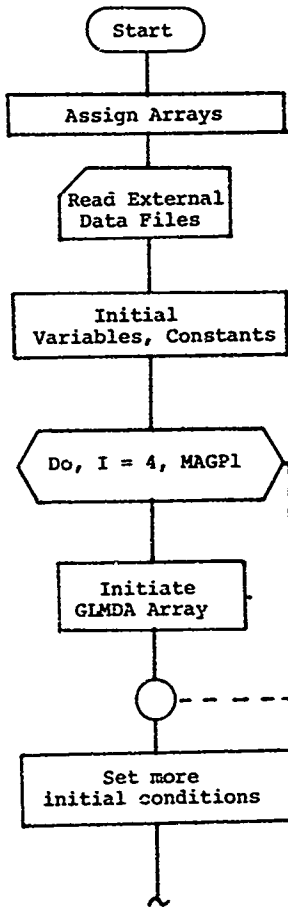
An exact calculation over all  $\gamma$  subintervals and data intervals involves about 16 hours on the PDP 15/40. With  $XER=2.0$ , the time is reduced to about 4 hours while on using the SXER technique the time is about 1.5 hours. This is a valuable saving in computer time. No significant difference in the results is obtained between these three methods.

The initial debugging and program development of this program and the equilibrium program was done in an interactive mode over several years on a H-635 and DTSS (Dartmouth Time

Sharing System). The results described would have been impossible to achieve without this computer service where 50 or more short runs could be accomplished in one's own office in two hours. Once debugged the programs were shifted to the PDP 15/40 for the long runs. The accuracy could also be checked as 7-8 digits are significant on the H-635 while only 5-6 digits are significant on the PDP 15/40. Using double precision on certain quantities, closely similar results were obtained with the two computers.

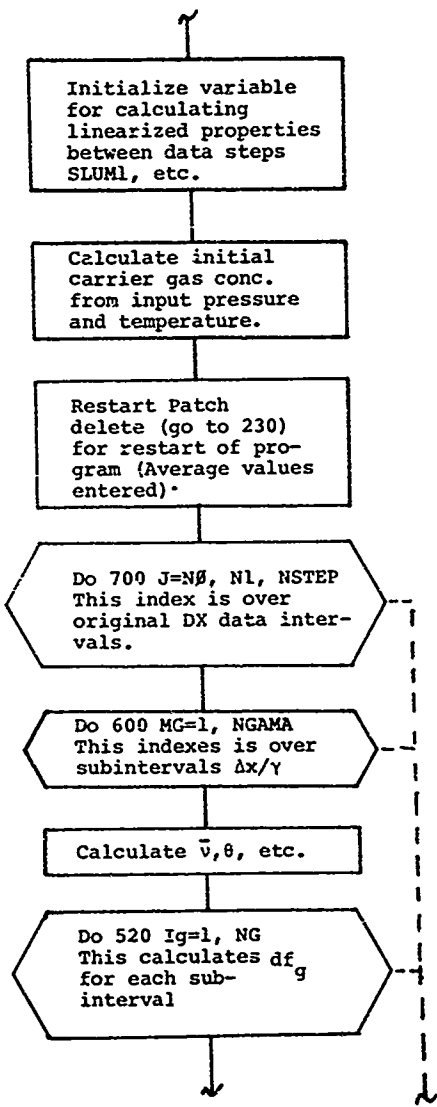
Another feature that should be mentioned is the restart capability. If for some reason a run is terminated before completion, it can be restarted with loss of, at most, less than one data interval of computation. The restart is not precise since only average values of the nozzle geometry are used (see RESTART PATCH), however, if for some reason long runs become infeasible, the restart information could be fed into the initial file (OUTFIL SRC) each time NSTOP is reached (Statement 514 + 1).

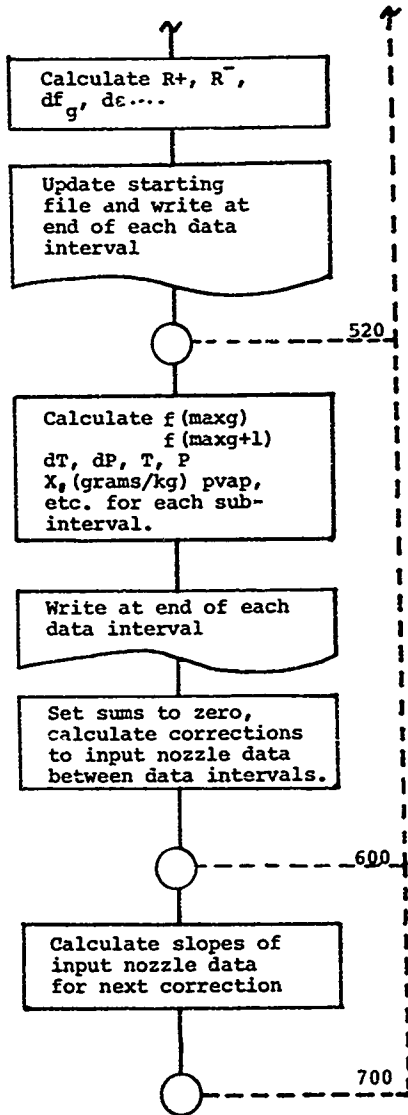
When NSTOP is reached the value of all cluster reaction terms ( $R_g^+$ ,  $R_g^-$ ,  $R_{g+1}^+$ ,  $R_{g+1}^-$ ,  $df_g$ , etc.) and flow properties ( $p/p_{01}$ ,  $T/T_{01}$ ,  $T^\circ K$ , etc.) are written out. Isentropic properties calculated by suppressing the reaction term of the expression for  $dT$ . (Equation V-2.7) are also reported. The partial pressure of the vapor obtained by summing the partial pressures of each cluster size is reported as PPAR.



FLOW CHART FOR COMPUTATION OF  
EVOLVING DISTRIBUTIONS

Figure VIII-3.1





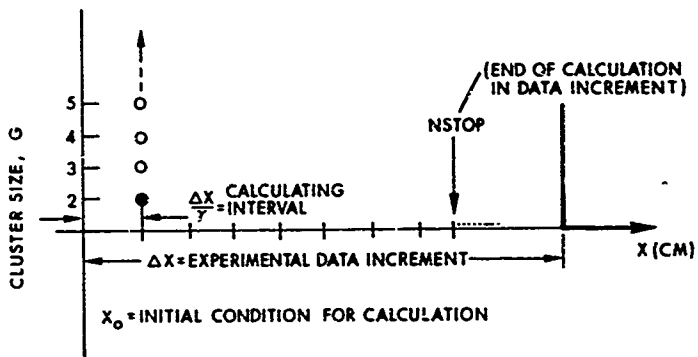


Figure VIII-3.2  
 Calculation Scheme for Each Data Interval



```

DOUBLEPRECISION  RHATZ, RHATZ2, DFGR, GRMS, SHGDFG,
&RTZ, RH1ZB1, RPL3B1, RPL3U, RPLUS, RH1NO, RPLCPI, PH1UP,
&SHGRG, SHMGFG, DFGE, DFG, PHATG, DFGBHL, DFCHL, DGL, DF, GLE,
&SUBRC, EXPT, DFGEK, DFGBEX, RHAT1, BRCPG, SUNGG, SHGRG, SUBGRG
REAL AC2)
DIMENSION CLNDA(20)
DIMENSION U(100), SCK(100), AREA(100), DADK(100), FOTK(20)
DIMENSION XNDA(2), XNDK(2), XNDK2(2), XNDK3(2), XOUTFI(2)
DATA XNDK(1), XNDK2(2), XNDK3(2), XNDK3(2), XNDK3(2), XNDK3(2)
DATA XNDK(1), XNDK2(2), XNDK3(2), XNDK3(2), XNDK3(2), XNDK3(2)
DATA XNDK(1), XNDK2(2), XNDK3(2), XNDK3(2), XNDK3(2), XNDK3(2)
DATA XOUTFI(1), XOUTFI(2), XOUTFI(2), XOUTFI(2), XOUTFI(2), XOUTFI(2)
DATA A-SHTAPEL, 4H SRC/
CALL ENTER(7, 8)
CALL SEEK(2, XNDK3)
E R BLOCK DIMENSION OF SHEFFIELD, ENCLDID, & A POURING, USIA,
CLV, & SHEFFIELD DIMENSION XY REVISED 3 DEC 1973
UNITS ARE CM, DEG, SEC, MOLECULE, MONOMER, CLUSTEP, DEG, KELVIN
READ(2, 100) N, X10, DELTAX, T01, PVAP, PAIR
DEFINE PVAP AS THE PARTIAL PRESSURE OF VAPOR AT XZERO
T01 IS THE STATIC VEMP AT X=0
READ(2 200) <SCK(1), U(1), AREA(1), DADK(1), J=1, N)
CALL CLOSE(2)
CALL SEEK(2, XOUTFI)
READ(2, 205) HXG, J, HO, PSTAT, PISEN, TDV15
READ(2, 211) F01H
READ(2, 211) F01U
READ(2, 211) F01D
READ(2, 211) F01X
MAXGPI=MAXGPI+1
READ(2 211) <FOTK(1G), IG=1, MAXGPI)
CALL CLOSE(2)
GLMIDAK(1)=0 0
GLMIDAK(2)=1 0
GLMIDAK(3)=2 0
GAMA= 5000
NGAMA=GGAMA
DLDC=0 0153
ASTOP=2000
WFAUG=9732
XNDK=3 35E12
TDK0=101
F01=76 2
CFO=0 480E-13
DO 220 I=4, MAXGPI
L=1
GLMIDAK(1)=GLMIDAK(L)+DLDC
CONTINUE
NG=J
IG=EP=1
HNUC=1
KI=JUNSTEP
RI=1 4E-08
RO=1 4E-08
PI=3 14159
XER=2 0

```

PI=3 14139

XER=2 0

XJ=J

GO TO 221

SKER=0 863

XERO=2 0

XEP=ZERO

STOP=HANA/XER

HSTOP=STOP

CONTINUE

EM=1 38E16

COIL=1 3E091

US1=U011U01

US11=U0111UFAC

US01=BX+400 0

US00=BX+106 0

GFAC=1 0

XN=1 250

REF=EXP(6 0+XN1)

REFUO=EXP(7 3)

U0110=U011

1DK00=273

XN00=3 3SE12

U000=U000GFAC

GRAD=SORTE 0

U1=5 3E-23

XN=5 3E-23

XN02=(2 2+XND/CR0+2.0+XN1)>>XN1

SIG02=FBARI

XN12=2 0+XN1/3.0

SIG12=1 95+R1

SIG11=2 0500+R1

SIG01=R1+R0

SIG101=SIG01+SIG11/2 0

SLU01=2200 0

DXCM=DELTAX

DZ=4 0+DXCM

DZ=6 0+DXCM

D00DY=C/DXCM(U00)-D0DXCM-1)/GAMA

DMU=12 0/GAMA

SLU=13 0\*(U(N0+12)-U(N0-1))/D1

4-C3 6\*(U(N0+2)-U(N0-2))/D2

4+(U(N0+3)-U(N0-3))/D3

DU=SLU+DXCM/GAMA

DEFINE RTAR=C1/RXDX/DX(U(J)), RTUJ=DU/DX

RTAR=35 6\*DXDX(K1)+U(K1)/AREAK1)

DELTAX=DELTAX/GAMA

DELTAX NOW CONTAINS GAMA INTERVALS

RTUJ AND F01M ARE THE INITIAL DISTRIBUTIONS OF MONOME

RTUJ MAY BE AT X ZERO. PLEASE NOTE

RTUJ=RTUJ

F1M=RTUJ/D1

F2M=RTUJ/D2

F01M=0 20E20

F11M=0 1492E+18

NG=MAXG

IF IS CONVERSION FACTOR TO GIVE P/P01 DIMENSIONLESS, ONCE 0

THE CONCENTRATIONS ARE KNOWN, IE P(G)/P01 = CP\*(K)\*TF

WE TAKE INITIAL VALUE OF DTM TO START, THEN CORRECT EA

```
DTM=DELTA*(X/K1)
N=1
DFG12=0 3E12
SUM1=0 0
XLGTDK=ALOG10(XNU0)/273.0
FOURPFSTAT (CF*EK*TDK)
GO TO 230
RESTART PATCH
DTH=0 446078695-09
DDSDX=0 19633276E-05
SLU=202 0582
DU=0 2020791E-01
SUM1=2331 0325
SUM1=2331 0325
RTU=1531 0335
RTU=2667 7861
DO 760 J=NO, NI, NSTEP
THIS DO INDEXES OVER ORIGINAL DELTAX INTERVALS
MBUC=0 THIS DO INDEXES OVER INTERVALS OF DELTAX/GAMA
DO 690 MG=1, NGAMA
DELTDK=TDK60-TDK15/10.
XLOG10=ALOG10(XNU0)-EXP(DELTDK*XNU)/REF
IF J=42/239, 230, 235
CL=10 240 3260-2507. 713/TDK15
CL=10 240
XLPIN=7 99039-(2022 003/TDK15)
CONTINUE
PIN=10 0+*XLPIN/10.0
CLINF=0 366E+20*PIN/TDK15
FIRST=XLGTDK*TDK15
SECHD=1 590*ALOG10(PIH/CLINF)
THIRD=SUM1/DFG12
SUM=FIRST+SECHD*3.02*THIRD
XNU=10 0+*(XLOGNU)
XNU1=XNU
NG1=NG-TDK
RT1=SORT(TDK/XM1)
RT1=SORT(TDK/XM1)
RT1=SORT(TDK/XM1)
Z11DD=211DD/2 0
Z11DD=5 89E-08*SORT(TDK)*SIG12+2*SORT(XNU12)
Z01DD=5 89E-08*SORT(TDK*XM1)*((XNU0*XM1)/XNU12)+
4SIG01+*2
Z6ZDD=5 89E-09*SORT(TDK*XNU02)*SIG02+*2
Z01DD=5 89E-08*SORT(TDK*XM1)*CANT02 0*XM1/
4CANT0*XM1)*SIG101E6 = RHATO
RHATO=PIH*(CANT0*RTU)
RH11D=PIH*(CANT0*RTU)
THETR=011/(EK*TDK)
THIS DO INDEXES OVER ALL SIZE G
DO 320 IG=1, NG
N=IG
MBUC=MBUC+1
G=IG
IF IG 20/382, 302, 303
```

```

10 ALPHA=1 0
11 GO TO 304
12 ALPHA=1 0 0.1*(G/GIHF)
13 CONTINUE
14 IF IG=23370,310,320
15 SECTION 310 TO 320 FOR SIZE G=2
16 XNG DEFINED EQUAL TO LAMBDA
17 CHIG=1 0
18 CHIGP=3 0
19 CHIGM=0 0
20 XNG=1 0
21 DELZ1=-1 0
22 GO TO 340
23 SECTION 320 TO 340 FOR SIZE G=3
24 CHIG=3 0
25 CHIGM=1 0
26 DELZ1=0 0
27 IF IG=32800,340,330
28 SECTION 330 TO 340 FOR SIZE G=4 AND UP
29 CHIG=3 0*(G-2, 0)
30 CHIGM= CHIG-3 0
31 XNG=3 0
32 DELZ1=0 0
33 FOLLOWING SECTION IS FOR SIZE G=1, DEFINE M=G+1
34 M=IG+1
35 G=1
36 IF IC=NG SKIP THIS SECTION AND SCRUB PREVIOUS (G+1)
37 VARIABLE NAMES ARE CHANGED INORDER TO SAVE THEM FOR PRINT
38 CHIGP=3 0*(G-2, 0)
39 ZP1=3 0*(G-20)*RT
40 RETURN NOW TO REGULAR G
41 G=IG
42 ZP1 DEFINED ABOVE
43 ZP2=ZP1
44 SIGNAL=1*(1, 0, G+0, 333)
45 XN1=XN1*(G/(1, 0, G))
46 XN2=XN2*(G/(G+0, XN1)*G)
47 ZIGDD=ZIG-SIGNAL*(Z-50*RT)
48 GO TO 490 FOR MONITOR COLLISION Z1 MUST BE HALVED
49 370 TO 372 ARE FOR G=1, ALL TIME
50 XNG=0 0
51 CHIG=0 0
52 CHIGM=1 0
53 CHIGL=0 0
54 CHIL=0 0
55 Z11=3 0
56 GO TO 492
57 LG=IG-1
58 IF (IG=37405, 410, 415
59 FOLLOWING SECTION IS FOR SIZE G=2
60 *(Z01DD*(F21V/ANUB1)
61 *(Z01DD*(F21V/ANUB1)
62 *(Z01DD*(F21V/ANUB1)
63 *(Z01DD*(F21V/ANUB1)
64 *(Z01DD*(F21V/ANUB1)
65 *(Z01DD*(F21V/ANUB1)
66 *(Z01DD*(F21V/ANUB1)
67 *(Z01DD*(F21V/ANUB1)
68 *(Z01DD*(F21V/ANUB1)
69 *(Z01DD*(F21V/ANUB1)
70 *(Z01DD*(F21V/ANUB1)
71 *(Z01DD*(F21V/ANUB1)
72 *(Z01DD*(F21V/ANUB1)
73 *(Z01DD*(F21V/ANUB1)
74 *(Z01DD*(F21V/ANUB1)
75 *(Z01DD*(F21V/ANUB1)
76 *(Z01DD*(F21V/ANUB1)
77 *(Z01DD*(F21V/ANUB1)
78 *(Z01DD*(F21V/ANUB1)
79 *(Z01DD*(F21V/ANUB1)
80 *(Z01DD*(F21V/ANUB1)
81 *(Z01DD*(F21V/ANUB1)
82 *(Z01DD*(F21V/ANUB1)
83 *(Z01DD*(F21V/ANUB1)
84 *(Z01DD*(F21V/ANUB1)
85 *(Z01DD*(F21V/ANUB1)
86 *(Z01DD*(F21V/ANUB1)
87 *(Z01DD*(F21V/ANUB1)
88 *(Z01DD*(F21V/ANUB1)
89 *(Z01DD*(F21V/ANUB1)
90 *(Z01DD*(F21V/ANUB1)
91 *(Z01DD*(F21V/ANUB1)
92 *(Z01DD*(F21V/ANUB1)
93 *(Z01DD*(F21V/ANUB1)
94 *(Z01DD*(F21V/ANUB1)
95 *(Z01DD*(F21V/ANUB1)
96 *(Z01DD*(F21V/ANUB1)
97 *(Z01DD*(F21V/ANUB1)
98 *(Z01DD*(F21V/ANUB1)
99 *(Z01DD*(F21V/ANUB1)
100 *(Z01DD*(F21V/ANUB1)

```

```

40 *EXP*(THETA*THETA*(1.0-EXP*(-THETA)))
    RFLUS=RPL3BI
    RM1IN=RM1ZBI
    RPLGDI=RP1FGTH<IG>*2.00<1.0-EXP (-GLNDK<IG>*THETA)>>/
    &(CHIG *CHIG -1 0))
    RM1UP=RM1SU
    GO TO 460

    FOLLOWING SECTION IS FOR SIZE G=3

410 RPLUS=RPL3BI
    RPLGDI=RP1FGTH<IG>*2.00<1.0-EXP (-GLNDK<IG>*THETA)>>/
    &(CHIG *CHIG -1 0))
    RPL4BI=RP1LQA
    RPL4BI=RP1LQA
    GLM=GLM
    DEFINE ALPPI=ALPHK*(G+1)
    XPM=4
    ALPPI=ALPHA
    RM1UP=2 *G*ALPPI*(XPM*FGTH<IN>)*EXP (-GLMTA)*
    &(1.0*GLMTA+0.5*GLMTA**2)
    &((CHIG<PI-1 0>)*(CHIG<PI-2 0>))
    RM1IU=RM1SU
    SUARRPL=SUARRPL*RP13BI
    SUARRP=RM1SU
    DELEP0=0011*GLMDK<IG>
    DELEP=DELEP0*BK*TDK*
    &(CRUSG 54*DELEZ1))
    SPKORG=SPKORG*DELEP*(RPLUS-RMIINU)
    DELTER=DELEP*(RPLUS-RMIINU)
    GO TO 470

    FOLLOWING SECTION IS FOR SIZE G=4 AND UP
    RPLUS IS FOR GROWTH INTO SIZE G FROM SIZE BELOW

415 RPI1=ZIGDD*P1TH
    RPLUS=RPLGPI
    RM1IN=RM1UP
    RPLGDI=RP1FGTH<IG>*4.00<1.0-EXP (-GLMDK<IG>*THETA)>>/
    &(CRUSG CHIG-1 0)*(CHIG-2 0))
    XPM=4
    ALPPI=ALPHA
    GLMTA=GLMDK<IN>*THETA
    RM1UP=2 *G*ALPPI*(XPM*FGTH<IN>)*EXP (-GLMTA)*
    &(1.0*GLMTA+0.5*GLMTA**2)
    &((CHIG<PI-1 0>)*(CHIG<PI-2 0>))
    GLMTA=GLMDK<IG>*THETA
    GO TO 463

420 ENTER G=2
    RMATZ=(RPLZBI-RMI2BI)*(&R13BI-RM1SU)
    P1CG=MATZ*10**XPM
    D1CG=DMATZ*10**XPM
    D1CG=C*DP66
    RMATZ=(RPL2BI-RMI2BI)*2.0
    SPKDFG=SPKDFG*G*DFG
    DELEP0=0011*GLMDK<IG>
    DELEP=DELEP0*BK*TDK*
    &(XMG+0.3**DELEZ1))
    SPKORG=DELEP*(RPL2BI-RMI2BI)
    DELTER=DELEP*(RPLUS-RMIINU)

```

```

DFG2=DFGA-DFGEX
DFG=DFG2
DFG2H1=DFG2
GO TO 499
ENTER G=4 & UP
CONTINUE
DELEP=J011*(ELMARCIG)
DELEP=(DELEP*(IG)/2.)*J011+DELEP
DELEP=DELEP*(KAY)DN*
&(MAG10.5*(DELZ1))
SUMG=SUMG-DELEP*(RPLUS-RMINU)
DELTER=DELEP*(RPLUS-RMINU)
ENTER G=3 & UP
RHAIG=(RPLUS-RMINU)-(RPLGP1-RMIUP1)
EXPT=FGTH(IG)*(STAR*RTUO)
DFGEX=EXPT*DTM*XR
DFGA=PRATGZ*DTM*XR
DFG=DFGA-DFGEX
GFC=G*RF*GH
SHDFC=SHDFT*DFG
SUMDFC=SUMDFC+GFC
SUMDFG IS STORED FROM G=1, ALSO SUMGG, BUTFITM IS ADDED
PRC=(C3*(G)-3*(B))*FGTH(IG)
SUMPPG=SUMPPG+PRC
SUMGG=SUMGG+GFG
ZINID=ZIGDD
ZINID=ZIGDD
THIS COMPLETES THE CALCULATIONS FOR CHANGES IN CONCENTRATIONS IN THIS SUBINTERVAL OVER ALL CLUSTER SIZES PRESENT
IN THIS SUBINTERVAL. THE CALCULATIONS ARE FOR ALL CLUSTERS BUT
BELOW THAT CONCENTRATIONS ARE CONSIDERED TO BE CONSTANT.
THIS IS BECAUSE WE NOW SAVE DFC FOR K(IG-1) WHILE COM-
ING. CHANGE WE NOW SAVE DFC BY CALLING IT DFCM1
ONE CHANGE AFTER COMPUTING THE NEXT HIGHER ONE
FITM MUST BE KEPT CONSTANT WITHIN ONE TIME INTERVAL
IT IS INVOLVED IN BIMOLECULAR PROCESS FOR ALL SIZE G
IN THAT INTERVAL. IT IS NOT CONNECTED UNTIL LEAVING
INTERVAL
IF(IG=3)505,503,504
F2TH=F2TH+DFG2H1
FGTH(2)=F2TH
GO TO 508
FGTH(IG)=FGTH(LG)+DFGHI
CONTINUE
DFGHI=DFG
CONTINUE
ZIG=ZIGDD+FITM*FGTH(IG)
COMPARE ZIG WITH ZINID. IF SAME GO ON
COMPARE ZIG WITH ZIGDD. IF SAME GO ON
SECTION BELOW IS USED TO STORE CONCENTRATIONS FOR
CALC DEVIATIVES FOR REST OF INTERVAL
CONTINUE
IF(CM=HSTOP)520,513,513
CONTINUE
IF(IG=HMXG)515,514,514
CONTINUE

```

```

CAL ENTER(2,XOUFI1)
WRITE(2,200)MAXG,KI,NO,PSTAT,PISEH,TDKIS
WRITE(2,211)FOTM
WRITE(2,211)FLOD
WRITE(2,211)TDK
WRITE(2,211)DOFX
WRITE(2,211)PGTKIGD,IG2=1,MANGP1)
ENDFILE 2
CONTINUE
WRITE(2,276)
IFIG=2016,316,317
DFG=3016
WRITE(2,277)D15,279D16,XCK(J+1),TK, DYSTAT,DFSTAT
WRITE(2,278)D16,PALUS,AMIKU,KILGFI,KTIUFI
WRITE(2,279)D16UC,FOTHKIGD,DFGG,DFGEX,DFG
CONTINUE
FOTM=MAXG*(FOTM+MAXG)+DFG
DFGFI=APLGP1-RH*F1-(FOTM+MAXGFI)*(RTAR+RTUU)>>*DTH+XER
FOTM+MAXGFI)=FOTM+MAXGFI
DFG=SUMDRC+3.0*FITH+3.5*E2H
DFGEX=FLTH*(RTAR+RTUU)*DTH+XER
DFG12=--SAGDFG-DFG1EX
DFG=DFG15
MAXRG12
FOTM1=FLTH
SUMGFG=SUMGFG+FLTH
FILTER=BK*TDK*(SAGDFG<DTH+XER)>>*(CHI+0.5*Z11+3/2)
S12=U11+2.1*SAGDFG<DTH+XER>
S12RG=SUMRG+FILTER
XIU1=SUMRG
XIU12=B*TDK*(FOTM+SUMGFG)<RTAR+RTUU>
XIU1N=XIU1-XIU12
C10=C10-BK
AZERO=C10
DENOM1=AZERO+PATH
DENOM2=BK*BK+C
DENOM3=DEKINEB*DENOM2
DELTA1=PSTAT<D1STAT*TDK-(RTAR+RTUU)*XER+DTH
PPAR=BK*TDK*(FOTM+CF
PPAR=BK*TDK*(C+S12RG+P01
S=PPAR/P1N
FLCIR=FLTH/CLINE
FCOEF=BK*TK+CF
TK=C
PSTAT=PSTAT+DFSTAT
DEFINE T ISENTROPIC = TDKIS
DEFINE P ISENTROPIC = PISEN
XNUMIS=BK*TDKIS*(FOTM+DTH)*(RTAR+RTUU)
DELTA=CCOEF*DENOM3+DTH
P1ISEN=XNUMIS/DENOM3+XER+DTH
TKIS=TKIS+D1ISEN
PISEN=P1ISEN+PISEN
DELTA1=TDK-TDKIS
DELTA2=PSTAT-PISEN
NOTE 0 IS DIMENSIONLESS
DUTH=S12RG/(C10+FOTM+T01)

```

DDDX=DODT\*UKJ  
DO=DODT\*XER\*DTH  
COF=X\*COF\*\*DQ  
COND=SUMGG  
GCP\*G=C\*V1\*XMO\* $\langle$ COID/FOTH $\rangle$ \*1000  
SUMGG=SUMGG\*FITH  
GBAP=SUMGG\*SUMGGF  
CIBP=ID\*9\*DK\*\*2 5\*SUMGG  
SUMGG=SUMGG  
FITH=15 IS RATIO OF INITIAL NUMBER TO TOTAL NO OF  
PAGES OF HQ. AT GIVEN LOCATION  
COF=COF+1  
XMO=XMO\* $\langle$ COID/COID $\rangle$ \*1E5\* $\langle$ SUMGG/FOTH $\rangle$   
RHOA=FOH\* $\langle$ RTAR\*RTUO $\rangle$   
DFO=RHATO\*XER\*DTH  
DF10D=RHAT1D\*XER\*DTH  
F10D=F10D\*DF10D  
RDTH=DTH\*XER  
SRDTH=SRDTH\*RDTH  
CONTINUE  
IF(NG-NSTOP)300,350,350  
CONTINUE  
WRITE(7,570)KI,XNUMR,XNUMI,XNUM2  
WRITE(7,570)NG,DEMOA,DEMOH1,DEMOH2  
WRITE(7,570)NG,DELTA,DELTA1,DELTA2,DDT  
WRITE(7,570)NG,PSTAT,PISEN,TDK1S  
WRITE(7,570)NG,DDX,DO,COFX  
WRITE(7,570)NG,GBAP,GBAPG,GBPKG,FOIH  
WRITE(7,7,J,F10D,DTH,SDTH,SMGRG,PPAR,C10,XHU  
WRITE(7,570)J,XER,RDTH,SRDTH  
WRITE(7,570)J,C10,XHU,THIRD  
WRITE(7,570)KI,FIRST,SECOND,SUM  
WRITE(7,570)KI,C10NF,S,PICR  
WRITE(7,260)  
SUM1=SUMGG  
ZIM100=0  
PPLUS=0  
RMINU=0  
SMGRG=0  
SUMGC=0  
SUMDF1=0  
SUMGG=0  
BRC=0  
SUMBRC=0  
SMGRG=0  
BRC=0  
BRC=0  
SUMDRX=SUMDRX\*DDDX  
SUMDDX=SUMDDX\*DDDX  
SUMDTC=SUMDTC\*SUMDRX  
SUMPL=SUMPL\*DU  
UM=UM\* $\langle$ J $\rangle$ \*SUMDU  
DUXXG=SLU\*SUMDU  
DAPK=35 6\*DAD\*NG\*DELTA  
AREAR=AREA\* $\langle$ J $\rangle$ \*DAHG  
RTAR=35 6\*DAD\*NG\*UMG/AREAR\*G  
FITH=DUXXG  
IF(NG-NSTOP)600,"90,800



```

590 CONTINUE
SUMD9=0 0
DAD9=0 0
SLDAD9=0 0
DRU=0 0
SUMPJ=0 0
DU=0 0
GO TO 620
CONTINUE
GO TO 621
XJ4=I
XJ4=I+SWR
STOP=COM/XER
NSTUP=STOP
621 CONTINUE
F1=N1+1
NRITE=NRITIC+1
DTM=DELTA/DX(UCK1)
SLDAD9=1 3 0*(DAD9(J+2)-DAD9(J))/D1
&+(3 0*(DAD9(J+3)-DAD9(J-1))/D2)
&+(DAD9(J+4)-DAD9(J-2))/D3
DAD9=SLDAD9*DELTA
SLU=C3 0*(UC(J+2)-UC(J))/D1
&+(3 0*(UC(J+3)-UC(J-1))/D2)
&+(UC(J+4)-UC(J-2))/D3
DAD9=SLU*DELTA
DAD9=SLU*DELTA
SLUMI=SLU
CONTINUE
CALL CLOSE(7)
STOP
600 FORMAT(110, E10.3, 4F10.5)
620 FORMAT(F10.5, F10.3, 2F10.5)
630 FORMAT(310, 3F10.5)
640 FORMAT(H, E16.9)
650 FORMAT(H, 310, 3F10.5)
660 FORMAT(16.9)
670 FORMAT(LUMI)
680 FORMAT(11, 15, 4E15.7)
690 FORMAT(1)
700 FORMAT(//)
710 STOP
END

```

0 5 58 7

|         |           |      |       |         |         |
|---------|-----------|------|-------|---------|---------|
| 0 00000 | 3352413   | 0 10 | 255 6 | 0 12661 | 0 04892 |
| 0 00000 | 17660 009 | 44   | 55357 | -0      | 0 05304 |
| 0 00000 | 17896 835 | 45   | 82546 | -0      | 0 05724 |
| 0 00000 | 19136 241 | 45   | 89543 | -0      | 0 06144 |
| 0 00000 | 19384 322 | 44   | 66312 | -0      | 0 06564 |
| 0 00000 | 19536 720 | 44   | 57182 | -0      | 0 06984 |
| 0 00000 | 19752 893 | 41   | 42187 | -0      | 0 07404 |
| 0 00000 | 19972 091 | 41   | 42187 | -0      | 0 07824 |
| 0 00000 | 19411 699 | 41   | 59472 | -0      | 0 08244 |
| 0 00000 | 19669 601 | 43   | 68559 | -0      | 0 08664 |
| 0 00000 | 19427 662 | 42   | 37344 | -0      | 0 09084 |
| 1 00000 | 20165 879 | 41   | 59167 | -0      | 0 09504 |
| 1 00000 | 20444 541 | 41   | 66379 | -0      | 0 09924 |
| 1 00000 | 20704 233 | 41   | 37391 | -0      | 0 10344 |
| 1 00000 | 20971 948 | 41   | 81529 | -0      | 0 10764 |
| 1 00000 | 21246 673 | 48   | 69650 | -0      | 0 11184 |
| 1 00000 | 21520 103 | 40   | 38848 | -0      | 0 11604 |
| 1 00000 | 21813 634 | 40   | 88812 | -0      | 0 12024 |
| 1 00000 | 22100 229 | 32   | 52133 | -0      | 0 12444 |
| 1 00000 | 22377 771 | 39   | 27144 | -0      | 0 12864 |
| 1 00000 | 22672 379 | 38   | 72583 | -0      | 0 13284 |
| 1 00000 | 22975 274 | 38   | 72583 | -0      | 0 13704 |
| 1 00000 | 23279 866 | 39   | 46639 | -0      | 0 14124 |
| 1 00000 | 23524 897 | 39   | 22164 | -0      | 0 14544 |
| 1 00000 | 24246 230 | 37   | 59414 | -0      | 0 14964 |
| 1 00000 | 24559 627 | 37   | 72822 | -0      | 0 15384 |
| 1 00000 | 24872 057 | 37   | 57800 | -0      | 0 15804 |
| 1 00000 | 25190 621 | 37   | 38763 | -0      | 0 16224 |
| 1 00000 | 25517 672 | 37   | 19360 | -0      | 0 16644 |
| 1 00000 | 25870 837 | 37   | 81401 | -0      | 0 17064 |
| 1 00000 | 26187 246 | 36   | 84653 | -0      | 0 17484 |
| 1 00000 | 26526 697 | 36   | 84653 | -0      | 0 17904 |
| 1 00000 | 26871 170 | 36   | 57913 | -0      | 0 18324 |
| 1 00000 | 27211 920 | 36   | 40883 | -0      | 0 18744 |
| 1 00000 | 27551 737 | 36   | 27432 | -0      | 0 19164 |
| 1 00000 | 27906 636 | 36   | 17556 | -0      | 0 19584 |
| 1 00000 | 28260 151 | 36   | 82623 | -0      | 0 20004 |
| 1 00000 | 28616 484 | 35   | 57113 | -0      | 0 20424 |
| 1 00000 | 28973 832 | 35   | 87335 | -0      | 0 20844 |
| 1 00000 | 29334 236 | 35   | 80009 | -0      | 0 21264 |
| 1 00000 | 29703 629 | 35   | 7115  | -0      | 0 21684 |
| 1 00000 | 30076 401 | 35   | 68701 | -0      | 0 22104 |
| 1 00000 | 30445 372 | 35   | 64519 | -0      | 0 22524 |
| 1 00000 | 30821 680 | 35   | 62562 | -0      | 0 22944 |
| 1 00000 | 31206 815 | 35   | 60333 | -0      | 0 23364 |
| 1 00000 | 31673 154 | 35   | 61008 | -0      | 0 23784 |
| 1 00000 | 32241 626 | 35   | 62934 | -0      | 0 24204 |
| 1 00000 | 32764 739 | 34   | 66305 | -0      | 0 24624 |
| 1 00000 | 33051 532 | 34   | 71107 | -0      | 0 25044 |
| 1 00000 | 33453 733 | 34   | 77167 | -0      | 0 25464 |
| 1 00000 | 33852 501 | 35   | 84740 | -0      | 0 25884 |
| 1 00000 | 34264 271 | 34   | 54134 | -0      | 0 26304 |
| 1 00000 | 34700 445 | 36   | 83371 | -0      | 0 26724 |
| 1 00000 | 35131 165 | 36   | 78277 | -0      | 0 27144 |
| 1 00000 | 35523 776 | 36   | 38227 | -0      | 0 27564 |
| 1 00000 | 35974 640 | 36   | 42392 | -0      | 0 27984 |
| 1 00000 | 36440 629 | 36   | 78080 | -0      | 0 28404 |

NONDAT SRC

|         |           |    |       |         |
|---------|-----------|----|-------|---------|
| 0 90000 | 36999 519 | 36 | 87143 | 0 04892 |
| 0 00000 | 37264 437 | 37 | 85372 | 0 05304 |
| 0 00000 | 37633 623 | 37 | 23202 | 0 05724 |
| 0 00000 | 38009 493 | 37 | 68772 | 0 06144 |
| 0 00000 | 38376 602 | 37 | 93323 | 0 06564 |
| 0 00000 | 38742 636 | 36 | 17831 | 0 06984 |
| 0 00000 | 39109 633 | 38 | 48803 | 0 07404 |
| 0 00000 | 39476 631 | 38 | 69631 | 0 07824 |
| 0 00000 | 40062 162 | 38 | 80990 | 0 08244 |
| 0 00000 | 40622 392 | 39 | 27352 | 0 08664 |
| 0 00000 | 40957 805 | 39 | 57750 | 0 09084 |
| 0 00000 | 41621 762 | 35 | 89387 | 0 09504 |
| 0 00000 | 41956 561 | 40 | 22131 | 0 09924 |
| 0 00000 | 42319 275 | 40 | 36274 | 0 10344 |
| 0 00000 | 42678 900 | 40 | 20402 | 0 10764 |
| 0 00000 | 43038 500 | 41 | 26402 | 0 11184 |
| 0 00000 | 43398 103 | 41 | 56643 | 0 11604 |
| 0 00000 | 43758 703 | 42 | 41974 | 0 12024 |
| 0 00000 | 44118 302 | 42 | 81519 | 0 12444 |
| 0 00000 | 44478 900 | 43 | 21894 | 0 12864 |
| 0 00000 | 44838 500 | 43 | 61684 | 0 13284 |
| 0 00000 | 45198 103 | 44 | 93875 | 0 13704 |
| 0 00000 | 45558 703 | 44 | 45600 | 0 14124 |
| 0 00000 | 45918 302 | 44 | 88269 | 0 14544 |
| 0 00000 | 46278 900 | 45 | 38056 | 0 14964 |
| 0 00000 | 46638 500 | 45 | 78978 | 0 15384 |
| 0 00000 | 46998 103 | 46 | 23280 | 0 15804 |
| 0 00000 | 47358 703 | 46 | 84417 | 0 16224 |
| 0 00000 | 47718 302 | 47 | 61953 | 0 16644 |

19

15 0 75000 0 75000 272 09990

0.20000000E+20  
0.16500000E+19  
0.27299990E+03  
0  
0.16000000E+18  
0.10299999E+15  
0.37157217E+13  
0.60335345E+11  
0.47734832E+09  
0.20333456E+07  
0.65337311E+04  
0.15731362E+02  
0.34739999E-01  
0.1923205E-04  
0.3420102E-06  
0.4373232E-09  
0.7874321E-12  
0.14039997E-17

OUTFIL SRC  
(HSC)

132

13 13 0.75683 0.75809 272.39990

- 18
- 209400002420
- 160000002418
- 272399908403
- 160000002410
- 102399902415
- 371372172413
- 14662399412
- 231693422410
- 300536762409
- 23091492406
- 743160712401
- 153755472401
- 132483302403
- 633343072406
- 263681352409
- 102376642410
- 343123012413

OUTFIL SRC  
(WCM)

APPENDIX 4

CORRIGENDA TO REF. (1)

TRANS. FAR. SOC. 65, 1267, 1969

$$\text{Equation 3.4 } \nu_{0,g} = g m_1 m_0 / (g m_1 + m_0)$$

$$\text{Equation 7.1+1 } (y_u)^g \quad (e/3g)^{3g}$$

$$\text{Equation 8.5 } K_g = (\sigma_{1,g}/r_1)^2 / (\nu_{1g}/m_1)^{1/2}$$

$$\text{Equation 8.8 } G(3,\theta) = 2.0(e^\theta - 1)/(1 + 2\theta)$$

$$\text{Equation 8.9 } G(g>3,\theta) = \{\exp[\theta(\lambda_g - 1)] - \exp[\theta(\lambda_g - \lambda_{g-1}^{-1})]\} / (1 + \lambda_g \theta + \frac{1}{2} \lambda_g^2 \theta^2)$$

$$\text{Equation 9.1 } R_1 = \sum_{g>2} (R_g^- - R_g^+) + 2 (R_2^- - R_2^+)$$