ACID RAIN: MICROPHYSICAL MODEL

By A. N. Dingle*

BASIC EQUATIONS

When HCl and H_2O vapors are present together, they jointly determine the equilibrium vapor pressure of each component over an HCl_{aq} droplet. It is assumed that the two vapors may be treated as if they diffuse independently. Thus, the change of mass of a solution droplet may be expressed as

$$dm_r = dm_1 + dm_2 \tag{1}$$

where the subscripts indicate the respective components; i.e., H_2O and HCl. Then, analogously with equation (1),

$$\frac{dm_1}{dt} = \frac{4\pi r D_1 F_{v_1} V}{R_1}\left(\frac{e_{a_1}}{T_a} - \frac{e_{r_1}}{T_r}\right) \tag{2}$$

and

$$\frac{dm_2}{dt} = \frac{4\pi r D_2 F_{v_2} V}{R_2}\left(\frac{e_{a_2}}{T_a} - \frac{e_{r_2}}{T_r}\right) \tag{3}$$

The energy balance of the droplet may be expressed by

$$Q_T = Q_L + Q_K + Q_R - Q_r + Q_M + Q_F + Q_D \tag{4}$$

*University of Michigan.

where Q_T, the internal energy increase, is defined as

$$Q_T = m_r c_r \frac{dT_r}{dt}$$

Q_L, the latent energy release, is defined as

$$Q_L = Q_{L_1} + Q_{L_2}$$

$$Q_{L_1} = L_1 \left(dm_1/dt\right)$$

$$Q_{L_2} = L_2 \left(dm_2/dt\right)$$

Q_K, the conductive heat transfer from drop, is defined as

$$Q_K = -4\pi r K F_K V \left(T_r - T_a\right)$$

Q_R, the radiative transfer from drop, is defined as

$$Q_R = -16\pi r^2 \sigma_R E T_a^{\,3} \left(T_r - T_a\right)$$

Q_r, the surface increase energy, is defined as

$$Q_r = 4\pi r^2 \left\{ \frac{2\sigma}{3} \left[\frac{1}{m_1} \frac{dm_r}{dt} + \frac{\mu}{\rho_r} \frac{\partial \rho_r}{\partial \mu} \left(\frac{1}{m_1} \frac{dm_1}{dt} - \frac{1}{m_2} \frac{dm_2}{dt} \right) \right] \right.$$

$$\left. -\mu \frac{\partial r}{\partial \mu} \left(\frac{1}{m_1} \frac{dm_1}{dt} - \frac{1}{m_2} \frac{dm_2}{dt} \right) + \frac{dT_r}{dt} \left(\frac{\partial \sigma}{\partial T} - \frac{2\sigma}{3} \frac{1}{\rho_r} \frac{\partial \rho_r}{T} \right) \right\}$$

Q_M, mixing, is defined as

$$Q_M = -c_r\left(T_r - T_a\right)\frac{dm_r}{dt}$$

Q_F, frictional conversion, is defined as

$$Q_F = \frac{2r^2 m_r g^2}{9\mu_f}\left(\rho_r - \rho_a\right)$$

and Q_D, the heat of dilution, is defined as

$$Q_D = \frac{\mu}{m_r}\frac{dh}{d\mu}\frac{dm_r}{dt}$$

A detailed discussion of the energy terms is given in reference 1 and need not be repeated here. A study of the relative magnitudes of these terms for different sizes of droplets of 4.0 molal HCl_{aq} in a 1-m/sec updraft (table I) shows that only Q_F is definitely negligible in the cloud droplet size range. This allows simplification of equation (4) to

$$Q_T = Q_L + Q_K + Q_R - Q_r + Q_M + Q_D \tag{5}$$

By means of the definitive expressions, the droplet temperature elevation may be written as

$$\left(T_r - T_a\right) = \left\{\frac{\left(Q_L + Q_D - Q_T - Q_r\right)}{\left[4\pi r\left(KF_K V + 4r\sigma_R E T_a^{\,3}\right) + c_r\frac{dm_r}{dt}\right]}\right\} \tag{6}$$

In addition, for each time step, the mass conservation accounts are kept. Assuming that there is no dilution of the air parcel by turbulent mixing with environmental air,

$$\frac{dx_1}{dt} = -\sum_i n_i \left(\frac{dm_1}{dt}\right)_i \tag{7}$$

$$\frac{dx_2}{dt} = -\sum_i n_i \left(\frac{dm_2}{dt}\right)_i \tag{8}$$

The environmental temperature and pressure changes from one time step to another are given by

$$\frac{dp}{dt} = -w\rho_a\left(g + \frac{dw}{dt}\right) \tag{9}$$

and

$$\frac{dT_a}{dt} = -\frac{\left[L_1 \frac{dx_1}{dt} + L_2 \frac{dx_2}{dt} + \left(g + \frac{dw}{dt}\right)\frac{dz}{dt}\left(1 + x_1 + x_2\right)\right]}{c_p + x_1 c_{p_1} + x_2 c_{p_2} + \sum_i \left(m_r c_r\right)_i n_i} \tag{10}$$

where the summation in the denominator represents the heat capacity of the liquid carried with the rising air parcel. Equations (2), (3), and (6) for each droplet size category and equations (7), (8), (9), and (10) constitute the explicit model for two volatile components.

NUMERICAL INTEGRATION TECHNIQUES

The numerical technique used for the integration of the microphysical equations is Hamming's modified predictor-corrector method started by a Rungë-Kutta procedure. This method has been described in reference 1 and is given in reference 2. At present, there are $2n + 2$ first-order ordinary differential equations to be solved simultaneously, where n is the number of droplet size classes. In terms of the variables used in reference 2, y_1' through y_n' are the derivatives with respect to time of the mass of water in a droplet in a specific size class:

$$y_1'\Big|_1^n = \frac{dm_1}{dt}\Big|_i$$

$$= \frac{4\pi r D_1 F_{v_1} V}{R_1}\left(\frac{e_{a_1}}{T_a} - \frac{e_{r_1}}{T_r}\right)$$

y_{n+1}' through y_{2n}' are the derivatives with respect to time of the HCl mass of a droplet in a specific size class:

$$y_1'\Big|_{n+1}^{2n} = \frac{dm_2}{dt}\Big|_i$$

$$= \frac{4\pi r D_2 F_{v_2} V}{R_2}\left(\frac{e_{a_2}}{T_a} - \frac{e_{r_2}}{T_r}\right)$$

y'_{2n+1} is the derivative with respect to time of cloud air temperature:

$$y'_{2n+1} = \frac{dT_a}{dt}$$

$$= \frac{L_1 \frac{dx_1}{dt} + L_2 \frac{dx_2}{dt} + \left(g + \frac{dw}{dt}\right) \frac{dz}{dt}\left(1 + x_1 + x_2\right)}{c_p + x_1 c_{p_1} + x_2 c_{p_2} + \sum \left(m_r c_r\right)_i n_i} \tag{11}$$

where n_i in the denominator on the right-hand side of equation (11) refers not to the number of size classes but to the number of droplets in size class i and where y'_{2n+2} is the derivative with respect to time of the cloud air pressure:

$$y'_{2n+2} = \frac{dp}{dt}$$

$$= -\left(\rho_a g \frac{dz}{dt} + \rho_a \frac{dz}{dt} \frac{d^2 z}{dt^2}\right)$$

The droplet distribution is initialized by assuming a starting pressure or height ($y_{2n+2}(0)$), temperature ($y_{2n+1}(0)$), relative humidity, and vapor pressure of HCl of the center of the cloud. The small droplets are assumed to be in equilibrium with the environment and the large droplets near equilibrium. Under these assumptions, the mass of H_2O ($y_1(0) \rightarrow y_n(0)$) and mass of HCl ($y_{n+1}(0) \rightarrow y_{2n}(0)$) on each droplet are determined. Integration of the microphysical equations now begins.

One of the benefits of the Hamming method is the fact that the local truncation error (LTE) is calculated at each increment of integration or time step and can be used to modify this time step. If the sum of the LTE's for each equation exceeds a given tolerance limit specified by the user, a new time step that is one-half the length of the previous time step is selected and the integration is restarted at the last accepted integrated values. This halving of the time step continues until the new values are within the error limit or until the number of halvings exceeds a specified limit. If the sum of LTE's is between the tolerance limit and one-fiftieth of the given tolerance limit, the calculated values are accepted and integration continues. Finally, if the sum of the LTE's is less than one-fiftieth of the given tolerance limit, the

calculated values are accepted, the time step is doubled, and the integration continues. With this time step adjustment, the integration is more accurate and efficient than if a fixed time step were used.

A computational instability was encountered during the integration of the microphysical equations. Some droplets were found to fluctuate wildly about their equilibrium values. The vapor pressures of HCl and H_2O in the environment may not equal the equilibrium vapor pressures at the droplet surface which are a function of temperature, molality, and radius. The existence of a vapor gradient allows the molality of HCl or H_2O (or both) independently of each other. The consequent condensation/evaporation of vapors may overcompensate the change in molality necessary for the droplet to reach equilibrium with the environment. The overcompensation of molality causes the vapor gradient to change sign, and during the next step, growth is in the opposite direction. To correct for the resultant instability or oscillation of the droplets about their equilibrium, the following scheme was developed.

Consider, for the moment, one diffusing vapor. The vapor difference at the droplet surface is some value B:

$$B = e_a - e_r$$

If the droplet goes to equilibrium, B goes to zero. The change of vapor difference for a droplet that goes to equilibrium during the time step is

$$B = -\left[\left(e_a - e_r\right)^{(t+\Delta t)} - \left(e_a - e_r\right)^{(t)}\right]$$

Grouping terms, one obtains

$$\left.\begin{aligned} B &= -\left[\frac{d}{dt}\left(e_a\right)\Delta t - \left(e_r^{(t+\Delta t)} - e_r^{(t)}\right)\right] \\ \Delta e &= B + d/dt\left(e_a\right)\Delta t \end{aligned}\right\} \qquad (12)$$

The vapor gradient is not allowed to collapse far beyond zero in a time step. Therefore, the change in vapor pressure Δe defines the maximum allowable change in vapor pressure. The maximum change in vapor pressure can then be used to find the maximum allowable change in droplet molality during a time step. The derivation of the maximum change in molality follows.

The vapor pressure to a droplet can be expressed as a function of droplet molality, temperature, and radius.

$$e = f(\mu, T, r)$$

Differentiating, one finds that

$$de = \frac{\partial e}{\partial \mu} d\mu + \frac{\partial e}{\partial T} dT + \frac{\partial e}{\partial r} dr \tag{13}$$

Having the equations for the vapor pressure of each component over a flat solution as a function of T and μ (ref. 1), it is an easy matter to differentiate and find that

$$\left.\frac{\partial e}{\partial \mu}\right|_{T,r} = A \tag{14a}$$

and

$$\left.\frac{\partial e}{\partial T}\right|_{\mu,r} = F \tag{14b}$$

Now, for a droplet of radius r, the vapor pressure at the surface is

$$e_r = e_{r=\infty} \exp\left(\frac{2\sigma}{\rho r R_v T}\right)$$

$$= e_{r=\infty} k$$

Then,

$$\left.\frac{\partial e}{\partial r}\right|_{T,\mu} = e_r\left(\frac{-2\sigma}{\rho r^2 R_v T}\right)$$

$$= -e_r \frac{k}{r}$$

Transforming $dr \rightarrow dm$, one obtains

$$\left.\frac{\partial e}{\partial r}\right|_{T,\mu} dr = -e_r \frac{k}{r} \frac{dm}{4\pi\rho r^2}$$

$$= G\ dm \tag{14c}$$

Substituting equations (14a), (14b), and (14c) into equation (13) yields

$$de = A\ d\mu + F\ dT + G\ dm$$

and in finite difference form,

$$\Delta e = A\ \Delta\mu + F\ \Delta T + G\ \Delta m$$

$$= B + \frac{de_a}{dt}\ \Delta T \tag{15}$$

From the definition of molality, one finds that

$$\Delta\mu = -\frac{\mu}{m_1}\ \Delta m_1 + \frac{\mu}{m_2}\ \Delta m_2$$

where m_1 is the solvent and m_2 is the solute.

The relative growth rate (dm_2/dm_1) can be determined from the growth equations (2) and (3):

$$\frac{dm_2}{dm_1} = \frac{\left(\frac{dm_2}{dt}\right)}{\left(\frac{dm_1}{dt}\right)}$$

Then,

$$\Delta\mu = \mu\left(\frac{1}{m_1} + \frac{1}{m_2}\frac{dm_2}{dm_1}\right)\Delta m_1 \tag{16}$$

Substituting equation (16) into equation (15) and solving for $\Delta\mu$,

$$\Delta\mu = \frac{B + \frac{d}{dt}\left(e_a\right)\Delta t - F\ \Delta T}{A + \frac{G}{\mu\left(-\frac{1}{m_1} + \frac{1}{m_2}\frac{dm_2}{dm_1}\right)}} \tag{17}$$

where $d(e_a)/dt$ and dT_a/dt are estimated by backward differencing. Then,

$$F\ \Delta T \simeq F\ \frac{dT_a}{dt}\ \Delta t$$

The maximum allowable change of molality determined from equation (17), $\Delta\mu_1$, applies to the solvent. Similar calculations for the solute result in another value, $\Delta\mu_2$. With the smaller value of the two, the maximum allowable values of Δm_1 and Δm_2 can be found in equation (16). This method is approximate.

However, one would not want to prevent the droplet from crossing the equilibrium line when the natural process is to do so. If the growth of the droplets becomes unstable, it will fluctuate wildly across the equilibrium line. Therefore, a domain about the equilibrium line is defined. If the droplet tends to grow and/or evaporate quickly outside that domain, it is assumed that there is a numerical instability. For the current computation, if the change of mass of either component computed by the numerical integration is less than three times the maximum allowable change estimated above, the integrated value is assumed correct. In practice, the factor of 3 is quite arbitrary; however, it is found that the ratio of calculated Δm to the estimated maximum allowable Δm is either $<<1$ or $>>10$. If the droplet growth is constrained in this manner, after the first few seconds on integration, only the two smallest size classes need adjustment and the model is stable.

RESULTS

To assess the situation in which droplet growth should be most favored, the microphysical model has been used to simulate the case of a ground cloud (GC) without dilution by entrainment and without precipitation. The updraft speeds used (table II) were chosen to approximate the observed behavior of several Titan ground clouds (ref. 3) as shown in figure 1. Thus, in this case, the GC reaches a height of 1000 meters at $t = 250$ seconds and stops rising after $t = 500$ seconds at a level of 1500 meters.

The initial GC temperature (at $t = 90$ seconds) is set at 25° C, and the initial HCl vapor pressure is 3.8 dyn/cm^2, corresponding to a concentration of 4 p/m at the 950-millibar level. The dry particle distribution was taken from the suggestion of Lala (ref. 4). It is a bimodal distribution of the following form.

$$\frac{dN}{d \log r} = \sum_{i=1}^{2} \frac{N_i \ \ln 10}{\sqrt{2\pi} \ \ln^2 \sigma_{gi}} \exp\left[- \frac{\left(\ln r - \ln r_{gi}\right)^2}{2 \ \ln^2 \sigma_{gi}} \right]$$

The various parameters suggested by Lala (ref. 4) are as follows.

$$N_2 = N_1/8000$$

$$\sum_{r=0.01}^{10} N = 1.5 \times 10^4 \text{ particles/cm}^3$$

$$\sigma_{g1} = \sigma_{g2}$$

$$= 2.0 \text{ micrometers}$$

$$r_{g1} = 0.05 \text{ micrometer}$$

$$r_{g2} = 1.0 \text{ micrometer}$$

The distribution is plotted in figure 2.

The course of the relative humidity H for the period 90 seconds $\leq t \leq 720$ seconds is shown in figure 3 for initial humidity values of 80, 90, and 100 percent. The effect of rapid initial droplet growth in the 100-percent case is to reduce the initial humidity quickly to a minimum of 98 percent at $t = 99$ seconds and then, with continued rising and cooling of the cloud, to approach the nearly constant value of 99.7 percent after 200 seconds. The asymptotic humidity value decreases by about 0.1-percent steps to the 90- and 80-percent cases.

Figure 4 shows the course of the HCl vapor pressure. It is reduced to 10^{-3} dyn/cm^2 at about $t = 300$ seconds for the 100-percent case, about 100 seconds later for the 90-percent case, and not until $t \simeq 500$ seconds for the 80-percent case. The droplet molalities decrease to 0.1 at $t = 225$, 300, and 500 seconds for the 100-, 90-, and 80-percent cases, respectively (fig. 5).

The droplet-size spectra after 720 seconds are shown in figure 6. The outstanding feature of this set of results is the enhancement of the growth of the largest droplets as the initial humidity is lowered. The curves are truncated at 7 micrometers, although the largest drops formed exceed 20 micrometers in radius. These are, however, very few in number. The bifurcation in the 100-percent relative humidity size distribution curve is an artifact produced in this case by the mechanics of calculating dN/dr. The equivalent cloud liquid water content figures at 720 seconds are, respectively, 2.8, 2.1, and 1.6 g/m^3 with mean droplet radii of 3.8, 3.75, and 3.4 micrometers.

An additional result of this study is that the droplet molalities are nearly constant across the size distribution at each value of t, a fact which will be helpful in parameterizing the microphysical processes for the submesoscale dynamic model. A summary of results at $t = 720$ seconds is given in table III.

REFERENCES

1. Dingle, A. N.: Rain Scavenging of Solid Rocket Exhaust Clouds. NASA CR-2928, 1978.

2. System/360 Scientific Subroutine Package (360A-CM-03X) Version 3 Programmer's Manual. International Business Machines Corp., Technical Publications Dept. H20-0205-3 (White Plains, N.Y.), 1970, p. 545.

3. Stephens, J. B.; and Stewart, R.: Rocket Exhaust Effluent Modeling for Tropospheric Air Quality and Environmental Assessments: Preliminary Report for NASA Space Shuttle Tropospheric Environmental Effects Meeting, Langley Research Center (Hampton, Va. 24026), Feb. 1975.

4. Lala, G. G.: First draft for Position Paper on the Potential of Inadvertent Weather Modification of the Florida Peninsula Resulting From Neutralization of Space Shuttle Solid Rocket Booster Exhaust Clouds, by E. Ballay, L. Bosart, E. Droessler, J. Jiusto, G. G. Lala, V. Mohnen, V. Schaefer, and P. Squires. Prepared for NASA Langley Research Center by Institute of Man and Science (Rensselaerville, N.Y.), Feb. 1978.

TABLE I.- ESTIMATES OF THE ENERGY TERMS

[In relation to Q_T for the HCl/H_2O system at $\mu = 4$]

Energy term	$r = 0.1\ \mu m$	$r = 1.0\ \mu m$	$r = 10\ \mu m$
Q_L/Q_T ($\approx Q_K/Q_T$)	1.46×10^4	4.28×10^4	1.95×10^3
Q_R/Q_T (E = 1)	.92	9.7	3.7
Q_r/Q_T	8.9	2.6	.012
Q_μ/Q_T	.006	1.05	.24
Q_F/Q_T	8×10^{-15}	1.2×10^{-12}	1.2×10^{-10}
Q_p/Q_T	94	276	13

TABLE II.- UPDRAFT SPEEDS AND HEIGHTS FOR STABILIZED GROUND CLOUD

Time, sec	Updraft speed, m/sec	Height, m
90 to 250	4	360 to 1000
250 to 500	2	1000 to 1500
500 to 720	0	1500

TABLE III.- VARIABLES AT TIME = 720 SECONDS

Variable	Initial humidity, percent		
	80	90	100
Temperature, K	290.99	292.45	293.73
Relative humidity, percent . . .	99.59	99.65	99.70
HCl vapor pressure, dyn/cm^2 . . .	0.001	0.001	0.001
Droplet molality	0.09	0.07	0.05
Liquid water content, g/m^3 . . .	1.56	2.14	2.80
Mean radius, μm	3.40	3.74	3.79
Standard deviation, μm	0.45	0.62	0.31
Largest droplet, μm	19.56	20.91	17.04

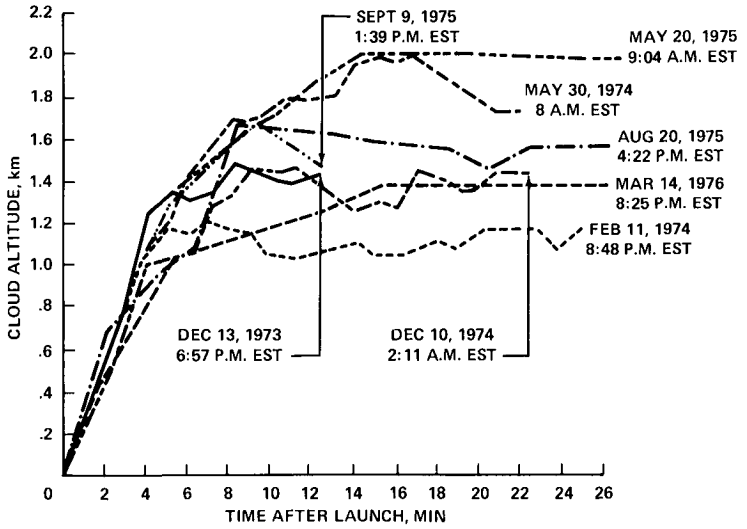

Figure 1.- Cloud rise and stabilization heights in eight Titan III launches.

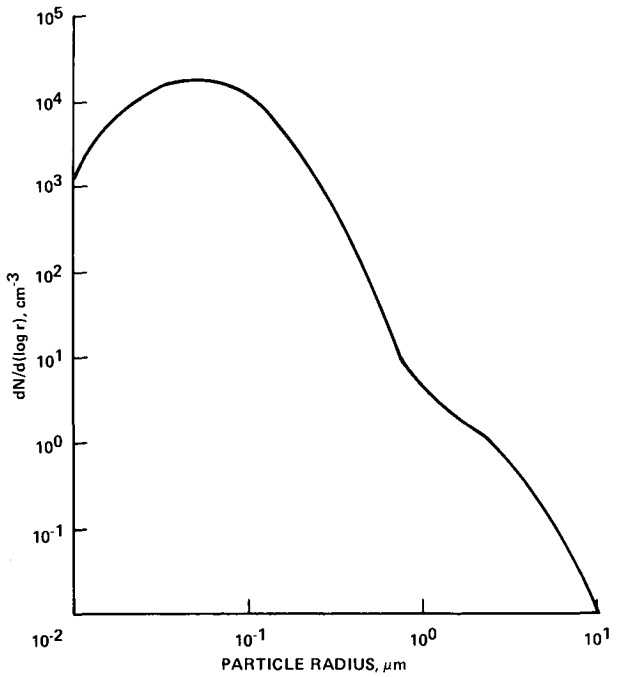

Figure 2.- Particle size distribution of Al_2O_3 in the ground cloud (after ref. 4).

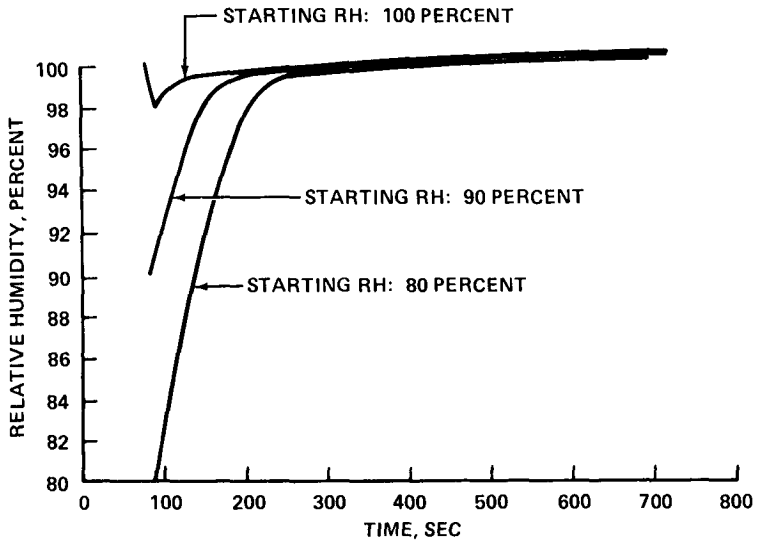

Figure 3.- Course of the relative humidity from $t = 90$ seconds to $t = 720$ seconds for initial humidity values of 80, 90, and 100 percent.

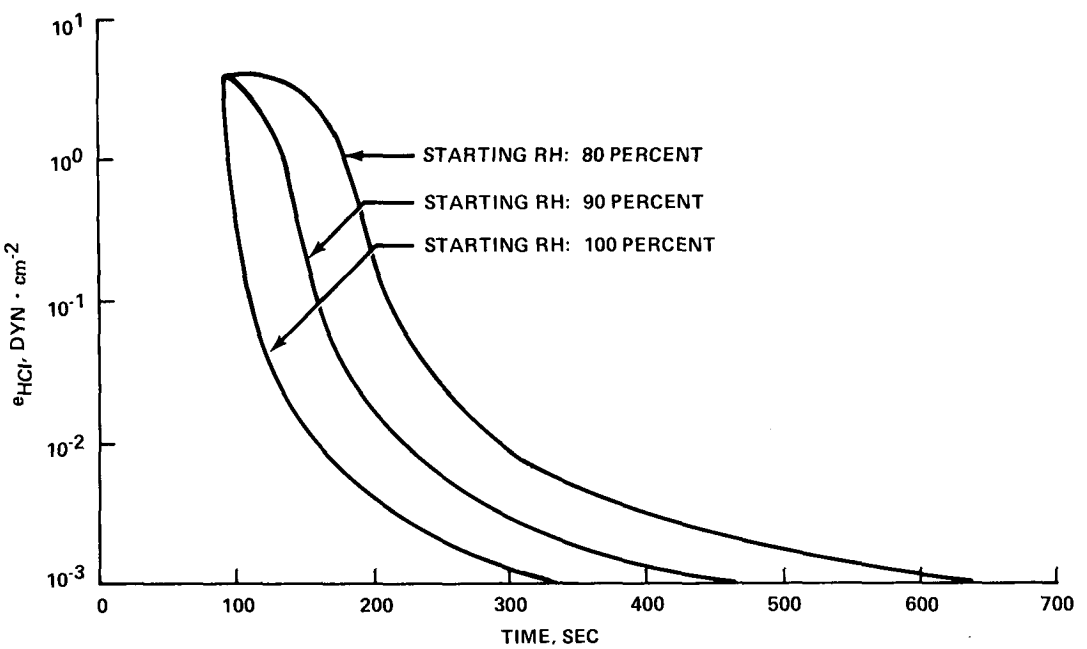

Figure 4.- Course of the HCl vapor pressure.

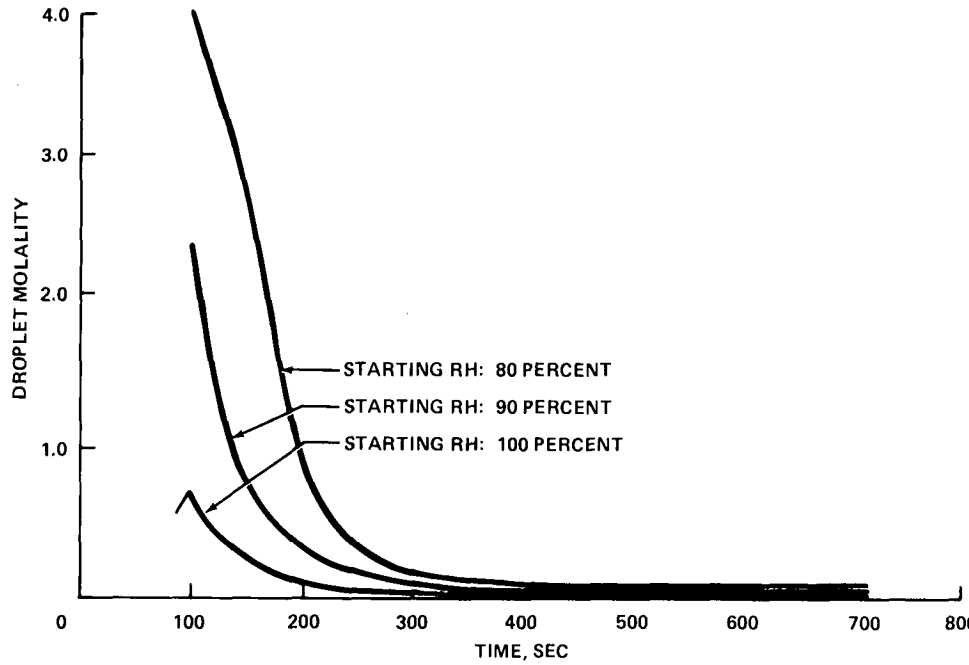

Figure 5.- Change of droplet molality with time.

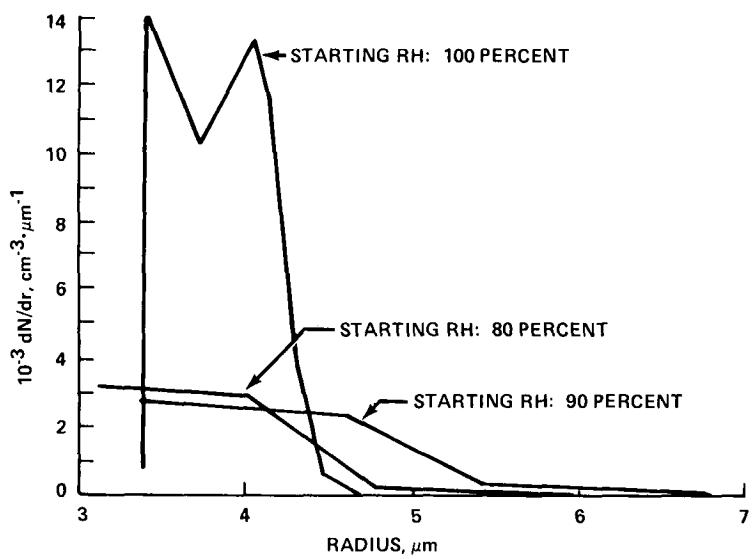

Figure 6.- Droplet-size spectra after 720 seconds (truncated at r = 7 micrometers).