

Possible Water Vapor Condensation in Rocket Exhaust Plumes

BENJAMIN J. C. WU*

Yale University, New Haven, Conn.

In an attempt to explain the observed radiance in the exhaust plume of an Apollo engine, the possibilities of any condensation by homogeneous nucleation under the conditions in the plume flowfield are examined. It was found that only H_2O could condense, the other species present in the exhaust, H_2 , remained unsaturated. Under the assumption of steady-state homogeneous nucleation, the accumulation of condensate as a function of the streamline coordinate has been computed from the Oswatitsch integral with empirical information gathered in previous experiments. Condensation is thus estimated to occur at about 45 m downstream of the nozzle exit. However, it has been found that the steady-state nucleation assumption may not be valid here, and the previous estimate may be too optimistic. Condensation under nonsteady homogeneous nucleation conditions would result in delayed condensation onset or none at all. A potentially useful alternative way of estimating condensation in plumes is outlined. Finally, keeping in mind that condensation may be induced by binary or heterogeneous nucleation, both of which favor earlier condensation onset, we conclude that condensation is not impossible in this exhaust plume.

Nomenclature

A	= stream tube area
c_v	= constant volume specific heat
g	= condensate mass fraction
J	= nucleation rate
k	= Boltzmann's constant
L	= latent heat of condensation
m	= molecular mass
M	= Mach number
n	= number of molecules in a cluster
N	= total number density of clusters
p	= pressure
q	= partition function
Q	= mass flow rate through stream tube
r	= radius
T	= temperature
u	= flow velocity
v	= molecular volume
x	= coordinate along the stream tube
y	= mole fraction
α	= mass accommodation coefficient
Γ	= correction factor, Eq. (1)
θ	= nonisothermal factor, Eq. (6)
ρ	= density
σ	= surface tension
τ	= characteristic time

Subscripts and Superscripts

c	= condensate
class	= classical
iso	= isothermal
noniso	= nonisothermal
r	= relaxation
rep	= replacement
rot	= rotational
tr	= translational
v	= vapor
∞	= bulk saturation properties
*	= critical cluster

Received May 22, 1974; revision received October 31, 1974. This work was supported by the Advanced Research Projects Agency, ARPA order 1179. The computer programs used here were developed under the support of the Power Program of the Office of Naval Research. The author wishes to thank P. P. Wegener of Yale University for cooperation and many fruitful discussions.

Index categories: Multiphase Flows; Jets, Wakes, and Viscid-Inviscid Flow Interactions; Spacecraft Tracking.

* Research Associate and Lecturer, Department of Engineering and Applied Science. Associate Member AIAA.

I. Introduction

WHEN a vapor undergoes adiabatic expansion, it may become saturated or even supersaturated, provided that the latent heat of condensation is greater than the enthalpy of the vapor, $L > c_p T$.¹ In the absence of sufficient foreign surfaces, condensation of the vapor is appreciably delayed, and considerable supersaturation may be required before actual phase change can take place. This nonequilibrium condensation is induced by nucleation, which may be homogeneous or heterogeneous depending on whether the nuclei are formed by the vapor molecules themselves or upon some foreign particles, e.g., aerosols such as smoke, dust, salt, ions, etc. The nucleation process is important here as it is the first indispensable step which leads to condensation. Adiabatic expansions of vapor with or without inert diluents which cause condensation have been observed in the operation of Wilson and diffusion cloud chambers, in supersonic flows in Laval and steam turbine nozzles, in high intensity molecular beams, in the rarefaction wave in the driver section of shock tubes, in Prandtl-Meyer expansions, etc.²

Another situation of practical interest where condensation may play an important role is the question of the origin of observed radiance of the high altitude, sun-lit rocket exhaust plumes outside the Earth's atmosphere. Here, the process is not the same as in the widely studied condensation phenomena of rocket exhausts or jets discharging into the atmosphere, the formation of condensation trails, etc., where turbulent mixing and vapor diffusion in a temperature gradient are the primary causes of condensation. The subject of this paper is to assess the possibility of condensation of certain species in the exhaust plume of an Apollo engine where such irradiance has been observed.

Homogeneous Nucleation†

Homogeneous nucleation theory is presently in a state of controversy^{3,4} over the energetics of cluster (condensation nucleus) formation whereas the classical steady-state kinetics^{5,6} of homogeneous nucleation is generally accepted. Moreover, in all variants of the homogeneous nucleation theory, the nucleation rate depends strongly on the questionable value of surface tension σ of extremely small clusters ($r \approx 5\text{\AA}$). Fortunately, the various models of the homogeneous nucleation theory, be it the "classical theory" based on thermodynamics^{5,6} or the "statistical

† As comprehensive reviews of this subject are readily available, references to the early, original papers are omitted here.

mechanical theory"⁷⁻¹¹ all retain the qualitative feature of an "onset of condensation," while differing seriously on the value of the "critical supersaturation" at which onset occurs. However, an unambiguous theoretical solution for the critical supersaturation is presently not available due to uncertainties in the surface tension of small clusters and energetics of cluster formation.

Condensation in Supersonic Nozzle Flows

Vapor condensation in supersonic nozzle flows has been studied extensively since the pioneering works of Stodola¹² with steam turbine nozzles, and Oswatitsch¹³ with wind tunnel nozzles. Since recent reviews are readily available,^{14,15} the phenomena will only briefly be described. Initially unsaturated vapor expands isentropically with accompanying temperature and pressure drop in the nozzle, and becomes saturated either in the subsonic or supersonic section. Owing to the high cooling rate prevailing in most nozzles (typically 10^5 to 10^6 °C/sec), condensation does not take place at saturation; instead, the vapor continues to expand and becomes supersaturated. Finally, condensation occurs in a catastrophic manner and the vapor returns to equilibrium. This sudden collapse of the supersaturated state is qualitatively well described with the notion of "critical supersaturation" in the theory of homogeneous nucleation. Quantitative agreement has not, however, been obtained unambiguously for all substances.

Experimental studies of condensation phenomena in supersonic nozzle flows are abundant and, in particular, condensation of water vapor has been studied extensively. Detailed measurements of H₂O condensation have been made using moist air,¹⁶⁻¹⁸ and using pure steam.¹⁹⁻²² Hill¹⁴ provided an authoritative critique of all the data available at that time. Onset of water vapor condensation has been determined in the temperature range $200 < T^* < 500$ K, and the pressure range $1 < p^*_{\text{H}_2\text{O}} < 3 \times 10^4$ torr. All these experiments correlate reasonably well with the classical theory of steady state homogeneous nucleation. If we express the nucleation rates as determined from static pressure measurements in these experiments by

$$J = \Gamma J_{\text{class}} \quad (1)$$

where the classical rate is given by

$$J_{\text{class}} = \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{p_v}{kT}\right)^2 \left(\frac{\sigma_\infty}{m_c}\right)^{1/2} v_c \exp\left(-\frac{4\pi r^*2}{3kT}\right) \quad (2)$$

with the critical radius defined as

$$r^* = 2\sigma v_c / [kT \ln(p_v/p_\infty)] \quad (3)$$

then we found²³

$$10^{-4} < \Gamma < 10^6 \quad (4)$$

depending on the temperature at onset point. Using in addition the nonisothermal correction factor θ for homogeneous nucleation theory derived by Feder et al.,¹¹

$$J_{\text{noniso}} = \theta J_{\text{iso}} \quad (5)$$

with

$$\theta = \frac{c_v/k + 0.5}{c_v/k + 0.5 + [L/kT - 0.5 - (1 - \partial \ln \sigma_\infty / \partial \ln T) \ln(p_v/p_\infty)]^2} \quad (6)$$

Barschdorff et al.²⁴ have shown that the lower limit on Γ is brought up to 10^{-2} . This nonisothermal treatment of nucleation kinetics accounts for the finite transfer rate of the latent heat of condensation from the clusters during their formative period, and it is important in condensation of pure vapors or in systems where carrier gas is not present in large quantities. In the moist air experiments of Pouring¹⁶ and Stein¹⁷ the water vapor is carried in an excess of air which contributes greatly to heat transfer, which makes the isothermal treatment of nucleation kinetics a good approximation. It was found^{17,21,23} that the onset point determined in these experiments (with $200 < T^* < 250$ K) can all be correlated by assuming $\sigma = \sigma_{\text{ice}}$ and $\Gamma \sim 10^6$. Thus, this may be regarded as an empirical correlation for the estimation of onset of condensation of moist air flows in supersonic nozzles.

The above discussion is based on the assumption that the nucleation rate may be computed from the steady state theory, while in expansions, the flow is unsteady in the Lagrangian framework. However, if the characteristic flow time τ_f of the vapor element is much longer than the build-up time τ_r of steady-state nucleation, one may assume that, once the fluid element reaches a new position along the nozzle and assumes a new thermodynamic state, the steady-state nucleation rate is instantly achieved. Therefore, the steady-state theory may be used to calculate the nucleation rate in this situation. The time of flight of fluid elements from saturation to onset of condensation may be taken as τ_f , while τ_r may be calculated from

$$\tau_r \sim \theta \frac{1}{4\pi r^*2} \frac{n^{*2}}{p_v/(2\pi m_c kT)^{1/2}} \quad (7)$$

which is implied in Kantrowitz's treatment²⁵ of nonsteady state nucleation theory. Typically, under conditions of Stein's¹⁷ experiments,† we have $\tau_f \sim 100$ μsec and $\tau_r \sim 1$ μsec . Thus, the quasi-steady-state assumption is justified for the calculation of nucleation rate in this instance.

Condensation in Molecular Beams

The situation is quite different for high intensity molecular beams issuing from nozzle sources. Here, extreme expansion of the test gas occurs in tiny nozzles ($0.1 < d < 1$ mm) and the total time of flight is usually of the order of microseconds. Beyond the nozzle, the gas eventually expands to such low pressures and temperatures that collisionless flow occurs, and these conditions are generally in the coexistence region. Condensation of the test gas may occur if its saturation line is crossed early in the expansion, well before the transition to collisionless flow. Then, collisions between the supersaturated gas molecules may cause clusters to form which will be practically "frozen" once the gas flow becomes collisionless. Experimental evidence of this phenomenon was first reported by Becker et al.²⁶ for A, N₂, and H₂. Since then, the families of noble gases and alkali metals, as well as N₂, CO₂, H₂, NO, etc., have been studied by many investigators.²⁷

Of special interest to us are the studies on water vapor by Leckenby et al.²⁸ using mass spectroscopy, and by Stein and Armstrong²⁹ using electron diffraction. All the experiments to date dealt with the size distribution of clusters or the structure of these clusters. Hence, the only information available is whether condensation has or has not occurred somewhere in the free jet flow but the location of the onset is not known. That steady-state nucleation theory is not applicable to the extremely fast expansions in nozzle beams has long been recognized,³⁰ since $\tau_f \lesssim \tau_r$ in these flows. Thus, results from molecular beams represent data taken under non-steady state nucleation conditions, in contrast to those from most supersonic nozzles operating at continuum conditions.

Considering the thermodynamic states accessible from a prescribed supply (source) condition and based on variations of expansion rates with nozzle size, etc., Hagena and Obert³¹ deduced a set of similarity scaling laws to correlate the source parameters (T_0 , p_0 , d) of the molecular beam flows that show the same condensation effects§ for a given gas. Moreover, in analogy to the law of corresponding states they introduced the notion of "corresponding jets" which enabled them to correlate a large number of experimental data of some noble gases, namely Ne, Ar, Kr, and Xe, where relatively large clusters ($\bar{n} \sim 10^3$ assuming singly ionized clusters) were observed. Their empirical scaling laws were partially corroborated by Golomb et al.³² However, the latter authors favored a three-body collision model for the formation of smaller clusters, and they deduced a scaling rule based on this model. This three-body picture appears to be intuitively correct, since it is necessary for a third body to

† Mach 1.8 nozzle, about 1 cm² throat area, 6 cm long, atmospheric inlet conditions.

§ By "same condensation effect" these authors mean the production of clusters with a specific mean size in the nozzle beams.

remove the excess energy during the formation of a dimer. In summary, data of condensation in high intensity molecular beam experiments with noble gases can be correlated reasonably well using Hagena and Obert's³¹ scaling rules when large clusters ($n \sim 10^3$) are formed whereas the modifications of Golomb et al.³² should be used when small clusters ($\bar{n} < 10$, say) are expected.

II. Condensation in Rocket Exhaust Plumes

Bowyer³³ was probably the first to study the possibility of homogeneous nucleation and condensation of water vapor as an explanation for the radiance of sun-lit rocket exhaust plumes. He applied Tolman's³⁴ theory of curvature effect on surface tension to the classical steady-state homogeneous nucleation rate equation, and used the approach of Oswatitsch¹³ to calculate the H_2O condensation rate in the exhaust plume of an unnamed rocket engine. For the conditions assumed for the flowfield, he found negligible condensation, and concluded that homogeneous nucleation could not have caused the scattering of sunlight observed. More recently, Hoffman et al.³⁵ used a similar approach to calculate the condensation rate of species like H_2O and CO_2 in the exhaust of bipropellant rockets. The purpose of their study was to estimate the effects of condensation on contamination of sensitive surfaces.

During the flight of Apollo 8 in late December 1968 extensive optical observation of the spacecraft was made.^{36,37} Particularly interesting are the series of photographs taken by the Smithsonian Astrophysical Observatory (SAO) in Hawaii when the translunar injection burn of the Saturn IVB engine took place. In these pictures, a bright region is seen in the wake of the rocket when illuminated by the sun. It has been suggested that light scattering of condensed particles in the exhaust plume may be responsible for this luminescence. Kung, et al.³⁸ made a detailed study of the SAO photographs by using stellar photometric standards and concluded that a cloud of about 10^9 H_2O particles/cm³ having an average radius of about 70–100 Å could cause sufficient sunlight to be scattered and registered on the film.

Analysis of the Apollo 8 Exhaust Plume Flowfield

Our study was undertaken to ascertain whether condensation by homogeneous nucleation was possible in this particular situation, if so, where in the plume the onset of condensation is to be expected. Table 1 lists the variations of pressure p , temperature T , density ρ , flow velocity u , and stream tube area A in the center stream tube in the plume flowfield of that Saturn IVB engine as functions of the distance from the exit plane of the nozzle. These data were calculated by Teare³⁹ and co-workers assuming chemically frozen, but vibrationally relaxing flow beyond the exit plane, and they are considered

Table 1 Variables in the center stream tube of the Apollo 8 exhaust plume flowfield^a

x (cm)	p (Torr)	T (K)	ρ (g/cm ³)	u (cm/sec)	A (cm ²)
169.5	125.4	1417	1.86×10^{-5}	4.170×10^3	3.010
199.7	83.37	1311	1.33	4.254	4.108
235.9	54.51	1202	9.53×10^{-6}	4.332	5.655
277.7	35.89	1101	6.849	4.401	7.745
325.7	23.78	1008	4.958	4.463	10.55
396.2	14.37	900.5	3.353	4.531	15.37
480.5	8.717	803.3	2.281	4.590	22.30
603.5	4.805	698.4	1.446	4.652	34.72
756.0	2.655	605.4	9.214×10^{-7}	4.704	53.86
1017	1.207	498.5	5.087	4.762	96.38
1417	0.4980	398.6	2.624	4.815	1.848×10^2
2117	0.1690	302.0	1.175	4.864	4.084
3788	0.03508	200.8	3.67×10^{-8}	4.914	1.294×10^3
10100	2.475×10^{-3}	100.8	5.158×10^{-9}	4.964	9.119
17320	5.765×10^{-4}	69.0	1.755	4.979	2.671×10^4

^a Data taken from Ref. 39.

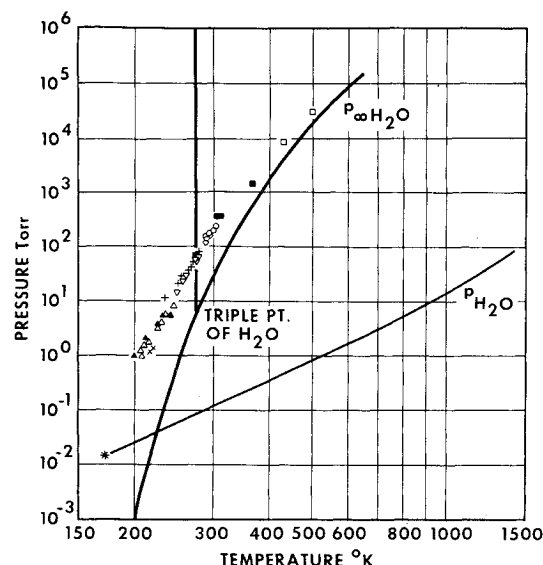


Fig. 1 Onset of water vapor condensation. *, calculated for this work, $\Gamma = 10^5$, steady-state theory. Experimental data and sources: \square , from Ref. 22; \blacksquare , Ref. 19; \circ , Ref. 21; \diamond , Ref. 44; $+$, Ref. 45; ∇ , Ref. 46; \triangle and \blacktriangle , Ref. 16; \times , Ref. 17.

good approximations to the real flow far downstream of the exit plane. The exhaust gas is a mixture of H_2 and H_2O , with constant mole fractions of 0.3071 and 0.6929, respectively. The partial pressure of H_2O , p_{H_2O} , is easily computed from Dalton's law and it is plotted in Fig. 1 as a function of temperature. The intersection of $p_{H_2O}(T)$ with $p_{\infty H_2O}(T)$, the saturation vapor pressure of water, marks the saturation of water vapor in the exhaust plume. This occurs at 225K, about 32 m downstream from the exit. Hydrogen remains unsaturated in the region of flowfield given. Assuming one-dimensional flow in the stream tube, the mass fraction of the condensate may be computed from the Oswatitsch integral¹³

$$g(x) = \frac{4\pi\rho_c}{3Q} \int_{x_0}^x J(\zeta) A(\zeta) r^3(x, \zeta) d\zeta \quad (8)$$

x_0 being the saturation point. Here, $r(x, \zeta)$ is given formally by

$$r(x, \zeta) = r^*(\zeta) + \int_{\zeta}^x \frac{dr}{dx} d\zeta \quad (9)$$

where dr/dx is the droplet growth rate. The nucleation rate in Eq. (8) is computed from the empirical relation, Eq. (1). The droplet growth rate is computed from the free molecular equation^{14,23} which accounts for the simultaneous heat transfer from the droplet. The free molecular assumption is satisfied here because the droplet radii are much smaller than the mean free path of the exhaust gas.

Results and Discussion

Equation (8) was integrated numerically in the flow direction using the gasdynamic conditions of the flow in Table 1. Figure 2 shows the accumulation of g along the center stream tube as a function of the empirical correction factor Γ here indicated in powers of ten. In these curves, the qualitative feature of onset of condensation is clearly exhibited with the sudden appearance of the condensate. This qualitative feature is also present in many observations in nozzle flows and it does not, of course, depend on the choice of Γ . The flow time of fluid elements originating at H_2O saturation is shown by the time of flight scale at the bottom of this figure. Defining the onset of condensation as the point where the mass fraction of condensate $g = 10^{-3}$, we plot the calculated point of onset in the center stream tube in Fig. 3 as a function of the correction factor Γ . This practical definition of onset was found useful in previous experiments with condensation of moist air^{17,46} pure stream^{40,45} and other sub-

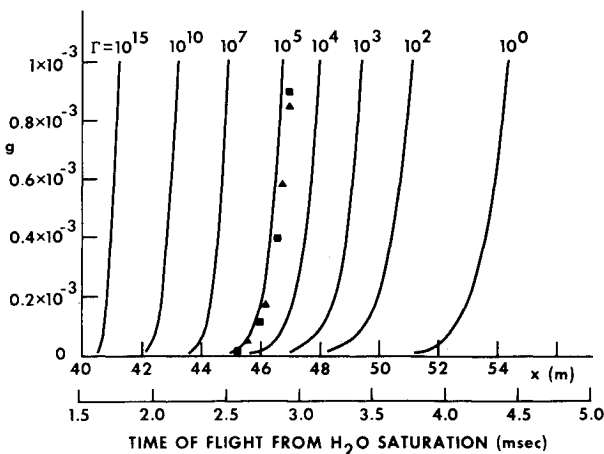


Fig. 2 Mass fraction of H_2O condensed in center stream tube of Apollo 8 exhaust plume. Steady-state nucleation, $\sigma = \sigma_{\infty ice}$. Solid curves, $\alpha = 1.0$; \blacksquare , $\Gamma = 10^5$ and $\alpha = 0.1$; \blacktriangle , 10^5 and 0.01 .

stances.⁴¹ In such work, light-scattering signals are detected once a cloud of droplets formed by homogeneous nucleation has attained roughly the quoted mass fraction. Moreover, due to the very nature of the onset of condensation the location of onset along x is not particularly sensitive to the value of g chosen for the definition of onset. For example, for the case $\Gamma = 10^5$ in Fig. (2), $g = 10^{-4}$ occurs at $x = 46$ m while $g = 10^{-3}$ occurs at $x = 47$ m. The theoretical limits for Γ are likely to be

$$1 < \Gamma < 10^{14} \quad (10)$$

where the lower limit corresponds to the classical theory. The upper limit is estimated⁴ from

$$\Gamma = \tilde{q}_{tr}^* \tilde{q}_{rot}^* / \tilde{q}_{rep}^* \quad (11)$$

where \tilde{q}_{rep}^* , the replacement factor, is given the value 10^3 as proposed by Lothe and Pound⁸ in their statistical mechanical model. The translational and rotational partition functions, \tilde{q}_{tr}^* and \tilde{q}_{rot}^* , are computed from well known formulas from statistical mechanics. This upper limit on Γ is much higher than the empirical estimate, a discrepancy found before for water vapor between Lothe and Pound's theory and experiments. Other models for \tilde{q}_{rep}^* (e.g. Dunning⁹) yield values of Γ that are much lower. However, we recall that none of the theories proposed is yet in a state to be applicable to engineering estimates. We note in Fig. 3 that the range $1 < \Gamma_{theory} < 10^{14}$ corresponds to the range $41 < x_{onset} < 55$ m calculated for steady-state homogeneous nucleation theories in the center stream tube. In view of this uncertainty, we shall simply use empirical knowledge gained in previous experiments.

Therefore, the choice of $\Gamma = 10^6$, $\sigma = \sigma_{\infty ice} = 96$ dyne/cm, and $\alpha = 1.0$ seems appropriate to estimate the onset of condensation of H_2O , when an excess of inert diluent is present. In the plume problem, however, we have $y_{H_2O} = 0.6929$, a high

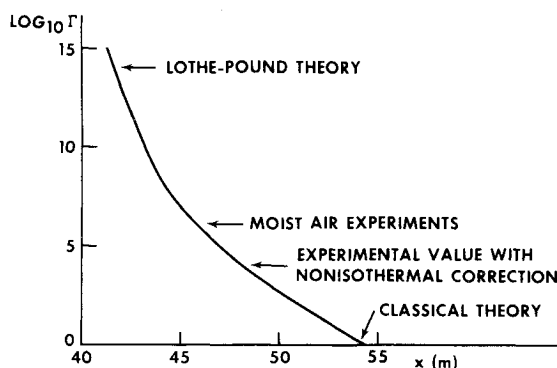


Fig. 3 Onset location as a function of Γ .

Table 2 Thermodynamic states at the onset of H_2O condensation

	Computed for plume with $\Gamma = 10^5$	Typical experiment condition ^a
p (Torr)	1.95×10^{-2}	219
p_{H_2O} (Torr)	1.35×10^{-2}	1.11
T (K)	173	214
M	12.8	1.36
$p_{H_2O} / p_{\infty H_2O}$	1500	120
r^* (Å)	3.6	4.4
n^*	6	11
N (cm ⁻³)	10^{10}	10^{13}

^a Data taken from Ref. 17.

value that calls for the nonisothermal kinetic treatment of nucleation. A simple calculation using Eq. (6) reveals that $0.02 < \theta < 0.024$, for $32 < x < 47$ m in the center stream tube. Hence, the nonisothermal nucleation factor is found to be a constant of the order of 10^{-2} . In other words the nonisothermal nucleation rate is only about 1% of the standard one, therefore we estimate $10^4 < \Gamma < 10^6$ for our problem. From these calculations, we finally find that condensation of water vapor may be expected in the plume at $x \approx 47$ m in the center stream tube, which is roughly 45 m downstream of the nozzle exit plane. Some thermodynamic variables at the onset of condensation computed for $\Gamma = 10^5$ are compared with typical experimental conditions in Table 2. The onset point is plotted in Fig. 1 together with the available data from nozzles. These results and comparisons reveal that the classical steady-state nucleation theory with empirical corrections predicts the condensation of H_2O in the plume at a pressure and temperature far removed from the region of available experimental data. This result may, however, be physically reasonable. Although onset temperatures of 170K are much lower than those obtained in previous nozzle experiments, evidence that water vapor can condense at temperature as low as 130K exists.⁴² Critical supersaturation of 10^3 as computed here are not uncommon.^{16,17} The effects of droplet growth rate on the onset point are found to be unimportant. This observation is borne out by Fig. 2 where the results of artificially changing the droplet growth rate by varying the mass accommodation coefficient in the range $0.01 < \alpha < 1.0$ in these calculations are also plotted. The data points for $\Gamma = 10^5$, $\alpha = 0.1$ and 0.01 are seen to follow closely the solid curve representing results for $\Gamma = 10^5$ and $\alpha = 1.0$ with the position of onset being practically unaffected.

Under the assumption that the stream tube area variation is not influenced by the heat addition to the gas stream resulting from condensation, calculations of droplet growth beyond the onset point were made for $\Gamma = 10^5$. The results show that at $x = 150$ m, $g = 0.105$. The droplet size distribution was calculated by following the growth process of particular classes of droplets as they are carried downstream by the gas flow. We estimate at $x = 150$ m, that the mass mean radius, $\bar{r} = 17$ Å (corresponding to $\bar{n} = 600$). Roughly 80% of all droplets fall in the size range of $15 < \bar{r} < 20$ Å, and 98% in $14 < \bar{r} < 21$ Å. The droplet size distribution is therefore very narrow, a qualitative feature found before from laser light scattering.⁴¹ Finally, the total number of droplets of all sizes, computed from

$$N(x) = \frac{\rho(x)}{Q} \int_{x_0}^x J(\zeta) A(\zeta) d\zeta \quad (12)$$

is found to be in the order of 10^{10} cm⁻³ at $x = 150$ m.

The weakest link in the preceding analysis may lie in the assumption of steady-state homogeneous nucleation. An examination of the thermodynamic state and flow variables in the supersaturated region reveals that the steady-state assumption may not be valid. The flow time τ_f from saturation to onset ($\Gamma = 10^5$) is about 3 msec along the center stream tube (Fig. 2). Yet the build-up time for steady-state homogeneous nucleation

under the existing thermodynamic conditions, estimated from Eq. (7), is about 14 msec. The value of the Damköhler parameter, τ_f/τ_r , is 0.2, cf. a typical value of 10^2 for condensation of H_2O in the nozzle¹⁷ quoted before. Since the condition $(\tau_f/\tau_r) > 1$ must be satisfied to insure a steady state cluster distribution, there is probably not enough time for the steady-state nucleation rate to be attained. The actual homogeneous nucleation rate may be lower than the steady-state rate used in these calculations. Hence, a calculation involving nonsteady homogeneous nucleation rate may yield onset of H_2O condensation further downstream from that found here, or in fact, it may predict no condensation at all. On the other hand, condensation by homogeneous nucleation cannot occur upstream of the onset locations found here. Conversely, had these calculations predicted no condensation, homogeneous nucleation could have been categorically ruled out as a possible process to explain the observed plume.

Thus, the major shortcoming of the calculations presented here is the inadequacy of the classical nucleation theory in dealing with nonsteady state situations. To overcome this difficulty one may use empirical knowledge of condensation obtained from molecular beam experiments which have roughly the same value for τ_f/τ_r . This approach was taken by Oman and Calia⁴³ who used the scaling laws of Hagena and Obert,³¹ and based their estimate of H_2O condensation on the experimental data available for N_2 and CO_2 . As these scaling laws correlate only those source conditions which will result in the formation of clusters of a certain mean size, Oman and Calia had to make further estimates about any additional droplet growth that might occur because of the more favorable supply conditions in the plume for condensation than the source conditions in the experiments. For $p_o = 50$ atm, $T_o = 4000$ K and $d = 39$ cm, Oman and Calia found the mean cluster size to be $\bar{r} \approx 90 \text{ Å}$ with $\bar{n} \approx 10^5$.

This estimate is, however, extremely sensitive to the supply temperature. Taking the supply conditions extrapolated from the conditions in Table 1 at constant η ratio of specific heats ($p_o = 12.2$ atm, $T_o = 5140$ K), we found different values; i.e., $\bar{r} \approx 8 \text{ Å}$ ($\bar{n} \approx 10^2$) using Oman and Calia's procedure.

The most serious uncertainty in Oman and Calia's⁴³ estimates may concern the application of simple scaling laws deduced for monatomic molecules to condensation of water, a substance with complex structure. In view of the vast range of extrapolation involved (from $d = 0.1$ mm to 39 cm, $T_o = 400$ K to 4000K, for experiment and plume, respectively), the present results from scaling law calculations are highly ambiguous. However, the procedure remains useful because the Damköhler parameter is implicitly taken into consideration here.

III. Summary and Conclusions

Onset of water vapor condensation in plumes induced by homogeneous nucleation has been calculated assuming steady-state nucleation theory for nonisothermal cluster growth and using empirical information gathered in numerous previous studies at higher temperatures and pressures. The results of this calculation show that H_2O condensation may take place about 45 m downstream of the nozzle exit plane in the center stream tube at a temperature of about 170K. Calculations of the condensation process beyond the onset point, using the stream tube area distribution of noncondensing flow lead to an estimate of the droplet size distribution. It is estimated that at $x = 150$ m in the center stream tube, about 10^{10} droplets/cm³ are formed by homogeneous nucleation. The mass mean radius of this cloud of droplets is about 17 Å.

[†] Note that Hagena and Obert's work is based on the assumption of constant ratio of specific heats. It is true that the actual expansion of the gas in the rocket nozzle does not take place at constant specific heats, and the extrapolated supply conditions are different from the actual ones. However, the extrapolated stagnation conditions serve to define a fictitious supply, from which a frozen, isentropic expansion of an ideal gas will lead to the flow described by Table 1.

It must be emphasized that the previous conclusions are derived from the crucial assumption of steady-state homogeneous nucleation. Further examination of the flowfield reveals that this assumption does not appear to be valid for the problem at hand. The build-up time for steady state homogeneous nucleation is estimated to be 14 msec while the relevant flow time is only 3 msec. Thus, it is seen that the flow is probably too rapid for the steady-state nucleation rate to be achieved. Consequently, H_2O condensation induced by homogeneous nucleation may occur at locations farther downstream than estimated or it may not occur at all. On the other hand, condensation by homogeneous nucleation cannot be ruled out at this time since the steady-state theory provides only the early limit for its occurrence.

The unsolved problem of time lag in nucleation may be circumvented by using similarity rules derived from and experimental data of H_2O condensation taken in high intensity molecular beam flows. In such experiments, the parameter relevant to nonsteady nucleation, the Damköhler ratio τ_f/τ_r , may be simulated. Empirical relations may then be used to scale the other parameters, geometrical dimensions, etc. to arrive at an estimate of the condensation effects in plumes. However, the theoretical work in the area is as yet incomplete and prediction of H_2O condensation is uncertain. More experimental work on H_2O condensation in molecular beams is needed before any empirical information useful for engineering estimates can be extracted.

We must finally emphasize that homogeneous nucleation is not the only mechanism capable of initiating H_2O condensation. The processes of heterogeneous and binary nucleation are also possible. These mechanisms both favor early phase change and they warrant intensive further study.

References

- Wegener, P. P. and Mack, L. M., "Condensation in Supersonic and Hypersonic Wind Tunnels," *Advances in Applied Mechanics*, Vol. 5, edited by H. L. Dryden and T. von Kármán, Academic Press, New York, 1958, pp. 307-447.
- Wegener, P. P., "Nonequilibrium Flow with Condensation," *Acta Mechanica*, in press, 1975.
- Anonymous, "Nucleation—That Factor 10^{17} ," *Nature*, Vol. 203, March 1971, p. 18.
- Wegener, P. P. and Parlange, J.-Y., "Condensation by Homogeneous Nucleation in the Vapor Phase," *Naturwissenschaften*, Vol. 57, Nov. 1970, pp. 525-533.
- Becker, R. and Döring, W., "Kinetische Behandlung der Keimbildung in übersättigten Dämpfen," *Annalen der Physik*, Vol. 24, Dec. 1935, pp. 719-752.
- Volmer, M., *Kinetik der Phasenbildung*, Steinkopff, Dresden and Leipzig, 1939.
- Kuhrt, F., "Das Tropfenmodell realer Gase," *Zeitschrift für Physik*, Vol. 131, Dec. 1951, pp. 185-214.
- Lothe, J. and Pound, G. M., "Statistical Mechanics of Nucleation," *Nucleation*, edited by A. C. Zettlemoyer, Marcel Dekker, New York, 1969, pp. 109-149.
- Dunning, W. J., "General and Theoretical Introduction," *Nucleation*, edited by A. C. Zettlemoyer, Marcel Dekker, New York, 1969, pp. 1-69.
- Reiss, H., "Treatment of Droplet Clusters by Means of the Classical Phase Integral in Nucleation Theory," *Journal of Statistical Physics*, Vol. 2, Jan. 1970, pp. 83-104.
- Feder, J., Russell, K. C., Lothe, J., and Pound, G. M., "Homogeneous Nucleation and Growth of Droplets in Vapours," *Advances in Physics*, Vol. 15, Jan. 1966, pp. 111-178.
- Stodola, A., *Steam and Gas Turbines*, translated from the sixth German edition, McGraw-Hill, New York, 1927, pp. 117-128, 1034-1075.
- Oswatitsch, K., "Kondensationserscheinungen in Überschall-düsen," *Zeitschrift für angewandte Mathematik und Mechanik*, Vol. 22, Feb. 1942, pp. 1-14.
- Hill, P. G., "Condensation of Water Vapor During Supersonic Expansion in Nozzles," *Journal of Fluid Mechanics*, Vol. 25, Pt. 3, 1966, pp. 593-620.
- Wegener, P. P., "Gasdynamics of Expansion Flows with Condensation, and Homogeneous Nucleation of Water Vapor," *Non-*

equilibrium Flows, Vol. 1, Pt. 1 of *Gasdynamics*, edited by P. P. Wegener, Marcel Dekker, New York, 1969, pp. 163–243.

¹⁶ Pouring, A. A., "Experimental and Analytic Investigation of Homogeneous Condensation of Water Vapor in Air During Rapid Expansions," D. Eng. thesis, Department of Engineering and Applied Science, Yale University, New Haven, Conn., 1963.

¹⁷ Stein, G. D., "Condensation of Ice Clusters by Homogeneous Nucleation from the Vapor Phase," Ph.D. thesis, Department of Engineering and Applied Science, Yale University, New Haven, Conn., 1967.

¹⁸ Jaeger, H. L., Willson, E. J., Hill, P. G., and Russell, K. C., "Nucleation of Supersaturated Vapors in Nozzles I.—H₂O and NH₃," *Journal of Chemical Physics*, Vol. 51, Dec. 1969, pp. 5380–5388.

¹⁹ Gyarmathy, G. and Meyer, H., "Spontane Kondensation," *VDI—Forschungsheft 508*, VDI-Verlag, Düsseldorf, 1965.

²⁰ Deych, M. Ye., Kurshakov, A. V., Saltanov, G. A., and Yatcheni, I. A., "A Study of the Structure of Two-Phase Flow behind a Condensation Shock in Supersonic Nozzles," *Energetika i Transport*, No. 2, 1969; English translation in *Heat Transfer—Soviet Research*, Vol. 1, Sept. 1969, pp. 95–105.

²¹ Barschdorff, D., "Verlauf der Zustandsgrößen und Gasdynamische Zusammenhänge bei der spontanen Kondensation reinen Wasserdampfes in Lavaldüsen," *Forschung im Ingenieurwesen*, Vol. 37, 1971, pp. 146–157.

²² Gyarmathy, G., Burkhard, H.-P., Lesch, F. and Siegenthaler, A., "Spontaneous Condensation of Steam at High Pressure: First Experimental Results," C66/73, Conference Pub. 3, Institution of Mechanical Engineers, London, 1973, pp. 182–186.

²³ Wu, B. J. C., "A Study on Vapor Condensation by Homogeneous Nucleation in Nozzles," Ph.D. thesis, Department of Engineering and Applied Science, Yale University, New Haven, Conn., 1972.

²⁴ Barschdorff, D., Dunning, W. J., Wegener, P. P., and Wu, B. J. C., "Homogeneous Nucleation in Steam Nozzle Condensation," *Nature—Physical Science*, Vol. 240, Dec. 1972, pp. 166–167.

²⁵ Kantrowitz, A., "Nucleation in Very Rapid Vapor Expansions," *Journal of Chemical Physics*, Vol. 19, Sept. 1951, pp. 1097–1100.

²⁶ Becker, E. W., Bier, K., and Henkes, W., "Strahlen aus kondensierten Atomen und Molekeln im Hochvakuum," *Zeitschrift für Physik*, Vol. 146, 1956, pp. 333–338.

²⁷ Hagena, O. F., "Cluster Beams from Nozzle Sources," *Gasdynamics*, Vol. 4, chap. 2, edited by P. P. Wegener, Marcel Dekker, New York, 1974.

²⁸ Leckenby, R. E., Robbins, E. J., and Trevalion, P. A., "Condensation Embryos in an Expanding Gas Beam," *Proceedings of the Royal Society (London)*, Ser. A, Vol. 280, Aug. 1964, pp. 409–429.

²⁹ Stein, G. D. and Armstrong, J. A., "Structure of Water and Carbon Dioxide Clusters Formed via Homogeneous Nucleation in Nozzle Beams," *Journal of Chemical Physics*, Vol. 58, March 1973, pp. 1999–2003.

³⁰ Andres, R. P. and Boudart, M., "Time Lag in Multistage Kinetics: Nucleation," *Journal of Chemical Physics*, Vol. 42, March 1964, pp. 2057–2064.

³¹ Hagena, O. F. and Obert, W., "Cluster Formation in Expanding Supersonic Jets: Effect of Pressure, Temperature, Nozzle Size, and Test Gas," *Journal of Chemical Physics*, Vol. 56, March 1972, pp. 1793–1802.

³² Golomb, D., Good, R. E., Bailey, A. B., Busby, M. R., and Dawbarn, R., "Dimers, Clusters and Condensation in Free Jets. II," *Journal of Chemical Physics*, Vol. 57, Nov. 1972, pp. 3844–3852.

³³ Bowyer, J. M., "Water Vapor Condensation as an Explanation for the Great Apparent Radiance of Sun-Lit High Altitude Rocket Exhaust Plumes," *Progress in Astronautics and Aeronautics: Heterogeneous Combustion*, Vol. 15, edited by H. G. Wolfhard, I. Glassman, and L. Green, Jr., Academic Press, New York, 1964, pp. 725–738.

³⁴ Tolman, R. C., "The Effect of Droplet Size on Surface Tension," *Journal of Chemical Physics*, Vol. 17, March 1949, pp. 333–337.

³⁵ Hoffman, R. J., Webber, W. T., Oeding, R. G., and Nunn, J. R., "An Analytical Model for the Prediction of Liquid Rocket Plume Contamination Effects on Sensitive Surfaces," WD-1963, Nov. 1972, McDonnell Douglas Astronautics Company—West, Huntington Beach, Calif.

³⁶ Liemohn, H. B., "Optical Observations of Apollo 8," *Sky and Telescope*, Vol. 37, March 1969, pp. 2–6.

³⁷ Lundquist, C. A., "Photometry from Apollo Tracking," *Space Research X*, edited by T. M. Donahue, P. A. Smith, and L. Thomas, North-Holland Pub. Co., Amsterdam, 1970, pp. 25–32.

³⁸ Kung, R. T. V., Cianciolo, L., and Myer, J. A., "Condensation in Apollo Translunar Injection Plume," private communication, Sept. 1973, AVCO-Everett Research Laboratory, Everett, Mass.

³⁹ Teare, J. D., private communication, Nov. 1972, AVCO-Everett Research Lab., Everett, Mass.

⁴⁰ Gyarmathy, G. and Lesch, F., "Fog Droplet Observation in Laval Nozzles and in an Experimental Turbine," *Proceedings 1969–70*, Vol. 184, Pt. 3G (III), Institution of Mechanical Engineers, London, 1970.

⁴¹ Clumpner, J. A., "Light Scattering from Ethyl Alcohol Droplets formed by Homogeneous Nucleation," *Journal of Chemical Physics*, Vol. 55, Nov. 1971, pp. 5042–5045.

⁴² Wegener, P. P. and Lundquist, G., "Condensation of Water Vapor in the Shock Tube below 150K," *Journal of Applied Physics*, Vol. 22, Feb. 1951, p. 233.

⁴³ Oman, R. A. and Calia, V. S., "Nonequilibrium Cluster Formation in Rocket Exhausts," RM-571, March 1973, Research Department, Grumman Aerospace Corp., Bethpage, New York.

⁴⁴ Binnie, A. M. and Green, J. R., "An Electrical Detector of Condensation in High-Velocity Steam," *Proceedings of the Royal Society (London)*, Ser. A, Vol. 181, 1943, pp. 134–154.

⁴⁵ Stein, G. D. and Moses, C. A., "Rayleigh Scattering Experiments on the Formation and Growth of Water Clusters Nucleated from the Vapor Phase," *Journal of Colloid and Interface Science*, Vol. 39, June 1973, pp. 504–512.

⁴⁶ Roberts, R., "A Light Scattering Investigation of Droplet Growth in Nozzle Condensation," Rept. 97, Feb. 1969, Gas Turbine Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.