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Effect of a Carrier Gas on Homogeneous Condensation in a Supersonic Nozzle

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The classical liquid drop theory for condensation was used in a computer solution to determine the effects of a carrier gas on homogeneous condensation. Zinc was used as the condensing vapor with helium, argon, or xenon as carrier gas in a nominal Mach 5 nozzle. It was found that the rate of accumulation of condensate is strongly dependent on the amount of carrier gas and can be rapidly increased by either increasing the mass fraction of carrier gas of low molecular weight or by decreasing the molecular weight of the carrier gas (for a given mass fraction). It was also found that for a change in nozzle angle of a factor of two, the area ratio at which the onset of condensation occurred changed very little. This was also true for a change in nozzle size (throat diameter) for a factor of two.

Nomenclature

A = nozzle area
C_p = specific heat of mixture in the stagnation chamber
g = mass fraction of condensed liquid
J = nucleation rate
k = Boltzman's constant
L = latent heat
$\dot{m}$ = mass rate of flow
N_A = Advogadro's number
p = pressure of the mixture
p_D = pressure at drop surface
p_v = partial pressure of the vapor
p_{v_s} = saturation pressure of the vapor corresponding to T
p_{z_o} = partial pressure of the vapor in the stagnation chamber
p_z = partial pressure of the zinc in the expanding mixture
p_o = pressure of the mixture in the stagnation chamber
r = radius of a liquid drop
r^* = critical drop radius
r' = the integrated value of dr/dx from the saturation point
R_u = universal gas constant
R^* = radius of the throat of the nozzle
S = the sum in the equation for g; defined in Eq. (24)
T = the gas temperature
T_D = the temperature of the droplet
T_s = saturation temperature corresponding to p_v
T_o = gas temperature in the stagnation chamber
u = gas velocity
x = distance downstream from the throat
Δx = increment in x used in S
y = initial mass fraction of the vapor in the stagnation chamber
α_c = thermal accommodation coefficient of the carrier gas
α_v = thermal accommodation coefficient of the vapor
δ = constant in Tolman's equation for σ [Eq. (13)]
μ_c = molecular weight of the carrier gas
μ_v = molecular weight of the vapor
ρ = total density of the mixture
ρ_L = density of the liquid
σ = surface tension
σ_∞ = surface tension of a flat surface
θ = nozzle half angle
ξ = a variable defining the point in the nozzle where a given drop was formed

Subscripts

i = indicates the current calculation point, x, in the nozzle
j = the integer assigned to each calculation point in the nozzle
k = the integer of the calculation point at $x - \Delta x_i$ (i.e., $k = i - 1$)

Introduction

In a supersonic nozzle the gas or vapor undergoes an isentropic expansion which results in a decrease in temperature and pressure. For most vapors, the saturation vapor pressure decreases with temperature faster than the static pressure does in a frozen (without phase change) isentropic expansion. Saturated conditions are therefore approached. In most cases, the expansion is rapid enough for the fluid to become considerably supersaturated and to enter a nonequilibrium state before any condensate if formed. Analyses of nonequilibrium condensation have been made for various cases and the theory has been summarized in several review papers.[1–3] However, all previous results have been confined to pure vapors or to extremely small fractions of vapor in a carrier gas. The problem of a vapor in a carrier gas where the two components are comparable fractions of the flow has not been previously considered. A treatment of the latter problem is presented here. The purpose of this analysis is to present results showing the effects of the quantity (mass fraction) of carrier gas and the molecular weight of the carrier gas on the condensation of the vapor.

Although it has been under increasing attack recently, the classical liquid drop theory was used for this study because it still seems to have the greatest success in matching experimental data from nozzle flows.[4–7] It provides a basis for comparison with, and extrapolation of, experimental data. It also provides in a qualitative manner prediction of the effects of different flow parameters on the condensation process. The theory yields a nucleation rate equation in terms of a critical drop size so that the value of the surface tension appears to the third power in the nucleation rate. Although there is some disagreement on surface tension correction for small radii, an adjustment can be made as a function of drop size through the Tolman[8] constant which was originally related to the intermolecular distance in the liquid drop. This modification seems to be generally regarded as reasonable[1,9,10] and is somewhat substantiated by experiment.[4,7] Experimental measurements of particle size[11] as well as previous studies,[7] were used to approximate a constant (0.53 Å) which appeared to be within the appropriate

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$$dA/dx = 2\pi \tan\theta(R^* + x \tan\theta) \tag{9}$$

These equations may be written in terms of p, g, and x, and dp/dx may be written in terms of dA/dx and dg/dx,

$$\frac{dp}{dx} = \frac{-(p/A)dA/dx + \{Lp/[T(C_p - gdL/dT_D)] - \dot{m}R_uT/(\mu_v uA)\}dg/dx}{1 - pA/(u\dot{m}) - puA/\{\dot{m}T(C_p - gdL/dT_D)\}} \tag{10}$$

limits. Conditions were chosen for which some experimental measurements were available. The solution is for flow through a conical nozzle with the onset of condensation restricted to taking place downstream of the sonic throat with no discontinuities in pressure (shocks) present. The solution was obtained using The University of Michigan IBM 360 computer.

Analysis

The basic assumptions made for the simplified model chosen are: 1) one-dimensional, steady, inviscid flow; 2) no external heat transfer; 3) the gases are perfect gases; 4) the liquid drops formed have the same velocity as the flow; 5) the liquid drops formed do not contribute to the pressure; 6) the volume of the condensed phase is negligible when compared to the total volume; 7) the vapor and its condensate are uniformly distributed; 8) changes in the entropy of mixing are neglected; 9) the heat of fusion is neglected.

It has been shown[2] that the flow equations based on these assumptions can be written

$$\rho u A = \dot{m} \tag{1}$$

or

$$d\rho/\rho + du/u + dA/A = 0 \tag{2}$$

$$\rho u du = -dp \tag{3}$$

$$p_v = \rho[(y - g)/\mu_v]R_uT \tag{4}$$

$$p = \rho[(1 - y)/\mu_c + (y - g)/\mu_v]R_uT \tag{5}$$

$$udu + C_p dT - d(gL) = 0 \tag{6}$$

or

$$u^2/2 + C_p(T - T_o) - gL = 0 \tag{7}$$

For a conical straight walled nozzle

$$A = \pi(R^* + x \tan\theta)^2 \tag{8}$$

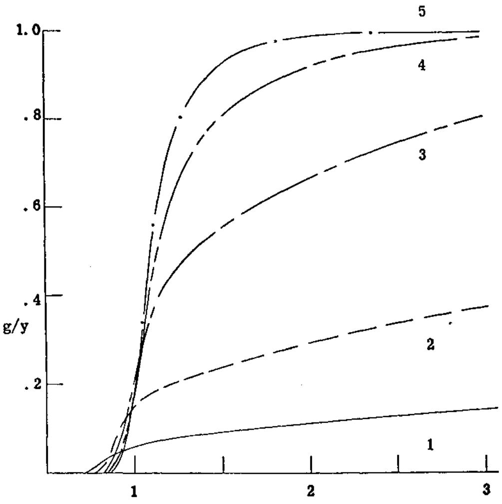

Fig. 1 Ratio of mass fraction of zinc condensate, g, to initial mass fraction of zinc vapor, y, as a function of distance downstream from the nozzle throat, x, and initial mass fraction of zinc in helium, for constant T_o = 2500 °K, P_{zo} = 882 psia. Curves 1, 2, 3, 4, 5 are for y = 1.0, 0.9, 0.7, 0.5, 0.3, respectively.

The classical equation for nucleation rate derived and discussed in Ref. 12 was used for the present calculations. The equation yields essentially the same result that other similar classical equations (such as those derived much earlier by Volmer, Becker, and Doering and others) yield. The assumptions inherent in the use of the equations[12] are the following: 1) drops are formed by spontaneous nucleation only; 2) only drops reaching the critical drop size can exist and grow or effect the flow; 3) the fact that the drops have an ordered velocity does not effect the nucleation process; 4) the drops are spherical; 5) the nucleation process is independent of the presence of the carrier gas (Ref. 13 includes a discussion of this); 6) thermodynamic equilibrium representation of the vapor properties with the nonequilibrium nucleation process is valid; 7) saturation pressure corresponds to saturation pressure of a drop of infinite radius; 8) the number of molecules of vapor is not decreased by the nucleation. The nucleation rate, J, which describes the number of critical size drops formed per unit volume per unit time is

$$J = \alpha_v\left(\frac{p_v}{kT}\right)^2 \frac{1}{\rho_L}\left[\frac{2\mu_v\sigma}{\pi N_A}\right]^{1/2} \exp\left(\frac{-4\pi\sigma r^{*2}}{3kT}\right) \tag{11}$$

where the critical drop size in terms of its radius is given by[12] the Thompson-Helmholtz equation,

$$r^* = \frac{2\sigma\mu_v}{\rho_L R_u T \ln(p_v/p_{v_s})} \tag{12}$$

As can be seen from Eqs. (11) and (12), J is a strong function of σ. As indicated earlier, an adjustment of σ for the drop radius was included in the analysis. This adjustment is

$$\sigma = \frac{\sigma_\infty}{1 + \delta/r^*} \tag{13}$$

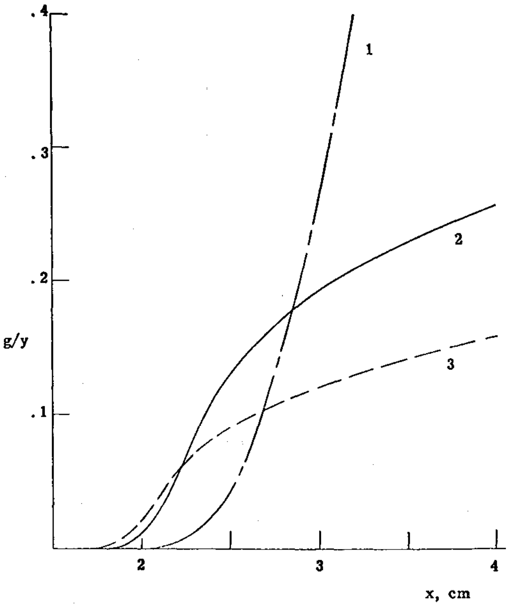

Fig. 2 Ratio of mass fraction of zinc condensate, g, to initial mass fraction of zinc vapor, y, as a function of distance downstream from the nozzle throat, x, and the molecular weight of the carrier gas at constant T_o = 2500 °K, P_{zo} = 144 psia, and y = 0.5. Curves 1, 2, 3 are for molecular weights of the carrier gas of 4.003, 39.95 and 131.3, respectively.

where σ_∞ is the surface tension of a flat surface and δ is a constant.

The equations used for the growth of critical size drops assume; 1) drop radius is much less than the local mean free path; 2) there is no agglomeration of the drops; 3) the gas mixture is composed of only pure vapor and pure carrier gas and contains no foreign substance; 4) the growth rate equation is valid when used with the steady flow approximation.

The equation for the growth of drops used to determine the effects of carrier gas was derived[6] from kinetic theory analysis of the number of molecules impinging on a unit area,

$$\frac{dr}{dx} = \frac{p_v}{\rho_L u}\left(\frac{\mu_v}{2\pi R_u}\right)^{1/2}\left\{\left(\frac{1}{T}\right)^{1/2} - \left(\frac{1}{T_s}\right)^{1/2}\right\} \tag{14}$$

This includes the additional assumptions that the effect of drop curvature on pressure may be neglected ($p_D = p_v$) and that since drops are formed at saturation conditions, the drop temperature equals the saturation temperature.

Having the relations for J and dr/dx the equation for g can be obtained. Consider any point downstream from the saturation point (i.e., the point at which the flow crosses the saturation curve). At this location drops will be in the process of being formed and there will be drops previously formed and in the process of growing. If this point is labeled x and the point at which a droplet originated is labeled ξ, then the radius of any drop at point x that was formed at point ξ is given by

$$r(x,\xi) = r^*(\xi) + \int_\xi^x \frac{dr}{dx}dx \tag{15}$$

where $\xi \leq x$. The mass of a drop formed at ξ is

$$(4\pi/3)\rho_L[r(x,\xi)]^3 \tag{16}$$

The rate at which these drops were formed in the interval $d\xi$ about ξ is

$$J(\xi)A(\xi)d\xi \tag{17}$$

Thus the mass rate of flow crossing x from the drops that were created at ξ is

$$(4\pi/3)\rho_L[r(x,\xi)]^3J(\xi)A(\xi)d\xi \tag{18}$$

This compared to the total rate of mass flux represents the mass fraction of these droplets. If, however, mass flow rate from all drops is calculated by considering the contribution from each point ξ. This, when compared to $\dot{m}$, is the mass fraction of condensate at point x. That is

$$g(x) = \frac{4\pi\rho_L}{3\dot{m}}\int_{xo}^{x}\{r(x,\xi)\}^3J(\xi)A(\xi)d\xi \tag{19}$$

where x_o is some point where $J = 0$. Taken here to be the saturation point.

A more convenient form of Eq. (19) is obtained by differentiating it and approximating the remaining integral. Performing the differentiation

$$\frac{dg(x)}{dx} = \frac{4\pi\rho_L}{\dot{m}}\left\{\frac{1}{3}J(x)A(x)\{r^*(x)\}^3 + \int_{xo}^{x}\{r(x,\xi)\}^2\frac{dr}{dx}J(\xi)A(\xi)d\xi\right\} \tag{20}$$

Noting that dr/dx is not a function of ξ since it is not a function of r but only of the particular point x, and approximating the integral by a sum, Eq. (20) becomes

$$\frac{dg}{dx} = \frac{4\pi\rho_L}{\dot{m}}\left\{\frac{1}{3}J(x)A(x)[r^*(x)]^3 + \frac{dr}{dx}\sum_{j=0}^{i} r_j^2J_jA_j\Delta x_j\right\} \tag{21}$$

where r_j, J_j, A_j, and Δx_j replace $r(x,\xi)$, $J(\xi)$, $A(\xi)$, and $d\xi$, respectively, and where i is the number of intervals each one corresponding to a width Δx_j that the distance $x - x_o$ is divided into.

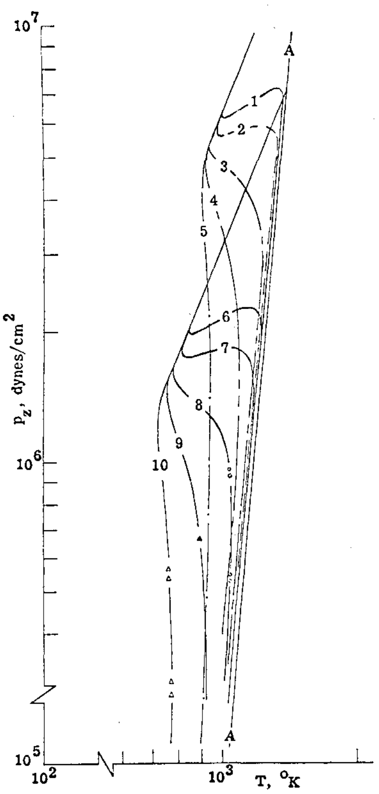

Fig. 3 Partial pressure of zinc, p_z, as a function of local temperature of the mixture, T, and initial mass fraction of zinc vapor, y. Curves 1, 2, 3, 4, 5 are for y = 1.0, 0.9, 0.7, 0.5, 0.3, respectively, with T_o = 2500 °K, P_{zo} = 882 psia, Curves 6, 7, 8, 9, 10 are for y = 1.0, 0.9, 0.7, 0.5, 0.3, respectively, with T_o = 4000 °K and P_{zo} = 1421 psia. Curve A is the equilibrium saturation line for zinc vapor.

Since dr/dx is not a function of r but only of x Eq. (15) can be integrated to give

$$r(x,\xi) = r^*(\xi) + r'_i(x) - r'_j(\xi) \tag{22}$$

where r'_i is the integrated value of dr/dx from the point x_o to x and r'_j is the integral of dr/dx from x_o to ξ. In terms of the above notation Eq. (22) is

$$r_j = r_j^* + r'_i - r'_j \tag{23}$$

Considering just the sum in Eq. (21) and substituting for r_j, we have

$$\sum_{j=0}^{i}(r_j^* + r'_i - r'_j)^2J_jA_j\Delta x_j \equiv S \tag{24}$$

where i goes from station x_o to station x and j goes from station x_o to ξ. If the point of interest, x, equals x_o this sum must obviously be zero. Defining S to be equal to the value of the sum at point x, i.e., up to i, and S_k to be the value of the sum at $x - \Delta x_i$, i.e., $i - 1 = k$, then their difference is

$$S - S_k = \sum_{j=0}^{k}[(r_j^* + r'_i - r'_j)^2J_jA_j\Delta x_j - (r_j^{*2} + r'_k - r'_j)^2J_jA_j\Delta x_j] + r_i^{*2}J_iA_i\Delta x_i \tag{25}$$

or expanding the squares and rearranging

$$S - S_k = r_i^{*2}J_iA_i\Delta x_i + \sum_{j=0}^{k} \times \{[(r'^2_i - r'^2_i) + 2(r_j^* - r'_j)(r'_i - r'_k)]\,J_jA_j\Delta x_j\} \tag{26}$$

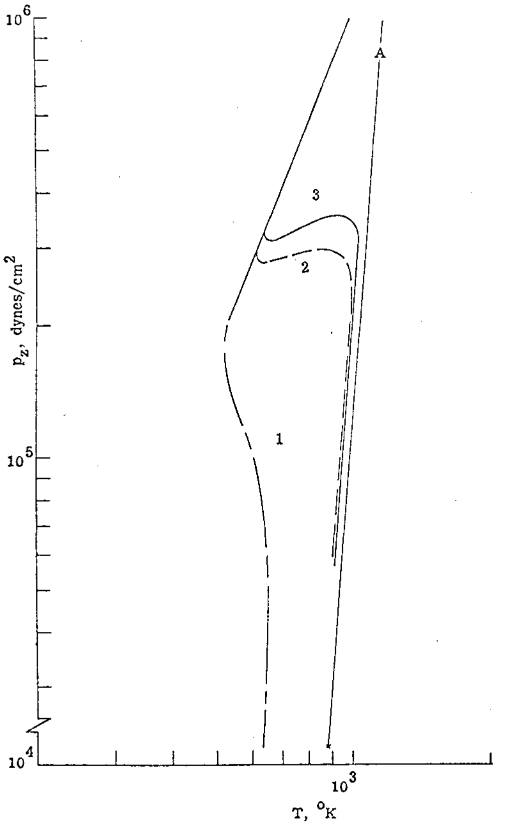

Fig. 4 Partial pressure of zinc, p_z, as a function of local temperature of the mixture, T, and the molecular weight of the carrier gas for $T_o = 2500$ °K, $P_{zo} = 144$ psia, $y = 0.5$. Curves 1, 2, 3 are for molecular weights of the carrier gas of 4.003, 39.95, and 131.3, respectively. Curve A is the equilibrium saturation line for zinc vapor.

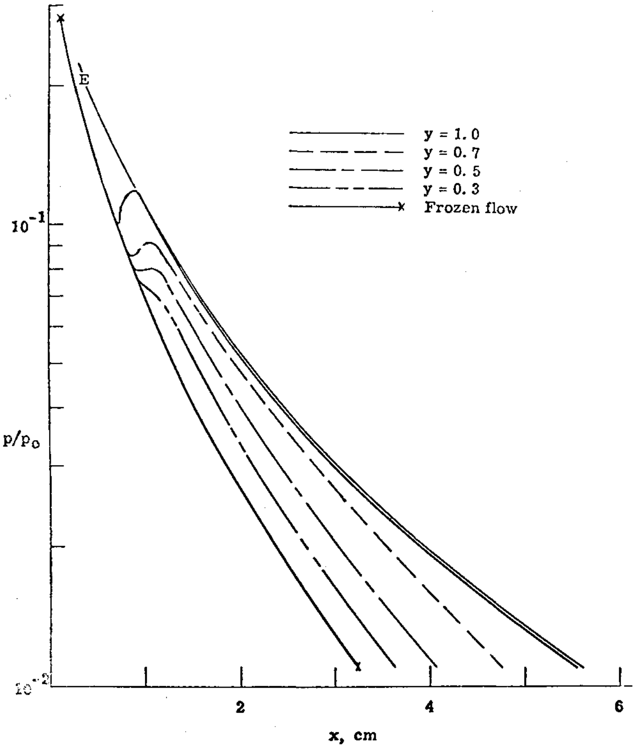

Fig. 5 Ratio of local pressure of the mixture, p, to the pressure of the mixture in the stagnation chamber, p_o, as a function of distance downstream from the nozzle throat, x, and the initial mass fraction of zinc vapor, y, for $T_o = 2500$ °K and $P_{zo} = 882$ psia. Curve E is for an equilibrium saturated expansion of pure zinc vapor ($y = 1.0$).

or since r'_i and r'_k are invariant with j

$$S = S_k + r_i{}^{*2} J_i A_i \Delta x_i + (r'^2{}_i - r'^2{}_k) \sum_{j=0}^{k} J_j A_j \Delta x_j +$$
$$2(r'_i - r'_k) \sum_{j=0}^{k} (r_j{}^* - r'_j) J_j A_j \Delta x_j \quad (27)$$

The two summations in Eq. (27) are easy values to compute, since they can be summed as the calculation goes from point to point downstream. This makes S an easy value to obtain in a calculation since it then becomes the sum of current values and the value it had at the last computation point. Using the subscript notation and substituting S in Eq. (21)

$$dg/dx = [4\pi\rho_L/\dot{m}]\{\tfrac{1}{3} J_i A_i r_i{}^{*3} + S dr/dx\} \quad (28)$$

which, when integrated with respect to x, yields g at any point in the flow. This completes the set of equations needed to describe the flow provided r' is simultaneously calculated by integrating dr/dx.

$$\frac{dr}{dx} = \frac{(1/\rho_L u)(2R_u/\pi\mu_v T)^{1/2}\,[\alpha_v p_v + \alpha_c p_c(\mu_v/\mu_c)^{1/2}](T_s - T)}{L + 2\alpha_v R_u T_s/\mu_v} \quad (29)$$

In the development of the nucleation, growth rate and mass fraction equations several physical properties were introduced as known quantities. These are functions of temperature and were represented as general curvefit equations to the empirical data.

For each solution, the flow is considered expanded isentropically from the throat and compared to the saturation curve to find the saturation point. The flow is further expanded calculating the amount of condensate using the nucleation and growth rate equations. The complete set of equations is solved for each increment Δx, in a point by point progression down the nozzle while simultaneously integrating dp/dx, dg/dx, and dr/dx. The integration routine chosen was a fourth-order Runge-Kutta method. The calculations, unless otherwise noted, were for a nominal Mach 5 conical nozzle with a 3.5° half angle, 6 cm long. Zinc was the vapor considered with helium, argon, or xenon as noncondensing carrier gas. Accommodation coefficients were taken as unity.

Results

The primary effects of the carrier gas appear to be the result of the carrier gas acting as a sink for the latent heat released by the condensation. That is, it acts to cool the flow. Therefore, for a carrier gas such as helium with a very high specific heat, the more carrier gas the faster the accumulation of condensate, once condensation has started. This can be seen in Fig. 1. Figure 2 shows similar results for constant mass fraction of carrier gas but different molecular weights. The figures show that the vapor can be made to condense faster by the addition of gas of a low molecular weight.

An additional effect of the carrier gas results from the change in velocity of the gas mixture before onset of condensation. The lower the molecular weight of the mixture at a given point in the nozzle, the higher the velocity. Therefore when helium is the carrier gas, a higher mass fraction of helium means a lower residence time in the nozzle, or a faster expansion, or delayed onset. This can be seen in Fig. 3. Figure 4 shows the same effect for constant mass fraction of carrier gas but different molecular weights. Figure 5 shows

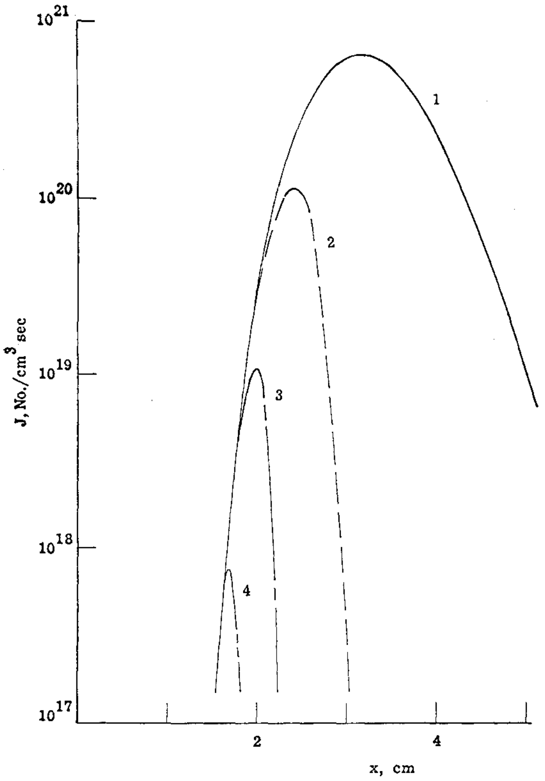

Fig. 6 Nucleation rate, *J*, as a function of distance downstream from the nozzle throat, *x*, using several different equations for particle growth rate, for T_o = 2500 °K, P_o = 2500 psia, y = 0.5. Curves 1, 2, 3, 4 were obtained using Eqs. (30, 14, 31, and 29), respectively.

the same effects in the $\bar{p}$-x plane. Changing the mass fraction of xenon makes almost no difference in the condensation process since the molecular weight of xenon is not different enough from that of zinc.

The effect of change in nozzle expansion angle was also considered. A change in nozzle cone half-angle from 7.5° to 3.6° made almost no change in the area ratio at which onset occurred. This was also true for a change in nozzle size. (The throat area, hence the scale of the expansion, was changed by a factor of four.)

To determine the effect of the equation for the rate of growth on the resultant solution, three other growth rate expressions were also considered. Figure 6 shows the nucleation rate as a function of location in the nozzle for four different growth rate expressions. Although the equation for growth changes the conditions at which onset of condensation occurs, the effects of the carrier gas obtained were qualitatively similar for any one given growth expression employed.

The three additional expressions for growth employed were:

$$dr/dx = (\alpha_v p_v / L\rho_L u)[2R_u/\pi\mu_v T]^{1/2}(T_s - T) \qquad (30)$$

$$dr/dx = 1/\rho_L u[\mu_v/2\pi R_u T]^{1/2}(p_v - p_{vs}) \qquad (31)$$

Equation (29) is the one derived by Stever[1] but modified to apply to the two-component case. Equation (30) is the latter equation with an accommodation coefficient of zero for the carrier gas, or the one component case as originally derived. Equation (31) is based on the kinetic theory model used previously for Eq. (14) assuming a sticking coefficient of one, but assuming that the drop temperature is equal to the gas temperature, as might be expected when the vapor represents only a very small fraction of the flow.

As can be seen from Fig. 6, the expression used for the growth of critical drops formed has a strong effect on where the collapse of supersaturation occurs which in turn determines the number of particles formed and the particle size. This suggests that with the attempts to obtain accurate expressions for the nucleation rate[14,15] there should be more attention paid to work on developing correct expressions for growth rate.

The main conclusions of the study are:

1) The higher the mass fraction of carrier gas of low molecular weight (helium) or the lower the molecular weight of carrier gas (at constant mass fraction), the faster is the accumulation of condensate after onset of condensation, but the greater is the supercooling and the smaller the particles far downstream.

2) The area ratio at which onset occurs is not very sensitive to the nozzle expansion angle (for a factor of two in nozzle angle) or to the change in nozzle scale (for a factor of two in nozzle scale).

3) Within the limitations of the present theory, the equation for rate of growth is easily as important as the nucleation rate equation in determining when the collapse of supersaturation occurs.

It should be noted that there is an unresolved controversy regarding corrections to the classical nucleation.[14–16] The corrected theories should yield similar relative effects of the carrier gas on the onset of nucleation, although actual onset points would differ for theories with different corrections.

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