

## CONDENSATION OF AMMONIA BY HOMOGENEOUS NUCLEATION IN SUPERSONIC NOZZLES

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(Received 10 June 1974)

**Abstract**—The problem of the condensation of ammonia, mixed with an inert gas (air or helium), during a supersonic expansion in a nozzle is studied theoretically. In the absence of particle coalescence phenomena, the condensation zone in a slowly divergent straight nozzle may be divided into a nucleation zone and a growth zone. A new formulation of the system of the differential equations which replaces the equation governing the condensate mass fraction is proposed. This formulation involves the calculation of quantities related to the description of the particle size distribution: the mean size, the number of particles per unit time, the second and third centered relative moments. The three latter quantities are conserved in the growth zone, leading to some substantial numerical advantages.

Profiles of the flow quantities, such as the condensate mass fraction and the particle-size distributions, are obtained in the case of a stationary one-dimensional flow. The influences of the value of the inert gas mass fraction in the nozzle reservoir, of the nature of the inert gas and of the form of the expression of the nucleation rate are examined.

Theoretical results are compared with experimental data and a good agreement is observed.

### INTRODUCTION

Condensation phenomena in thermodynamic conditions remote from an equilibrium state occur in many practical applications. The influence of a condensed phase on the flow of a vapor through a nozzle or between the blades of a wet steam turbine is of particular interest in the nuclear field. Indeed, pressurized water nuclear reactors, which constitute the most widely used nuclear energy sources for the near future, provide practically saturated steam at the first stages of a turbine. The presence of water droplets raises important problems of efficiency reduction, of corrosion, and erosion.

Condensation of a vapor, in mixture with an inert gas, is an important consideration in the design of supersonic and hypersonic wind tunnels, where the formation of droplets must be prohibited. In the same way in propulsion devices such as rocket exhaust nozzles which expand mixtures of condensable vapors and inert particles, the effects of condensation are significant.

Models for weather prediction rest on the understanding of the droplet formation which produces fogs and rain. Similarly, mathematical models of pollution depend on the description of two-phase condensing flows.

To clarify the understanding of a condensation process, the properties of the condensation zone of a vapor are studied in the simplest configuration, i.e. in a one-dimensional flow through a nozzle. Ammonia has been selected as a test fluid because its physical properties, such as the high value of the ratio of the latent heat of condensation to the specific heat, lead to a very clear illustration of the evolution of the flow quantities in the different parts of the condensation zone. Jaeger (1966), Kremmer & Okurounmu (1965) and Jaeger *et al.* (1969) have experimented on ammonia condensation, but principally in the presence of a low quantity of water vapor. The experimental data of Jaeger (1966) and Jaeger *et al.* (1969) tend to show that ammonia is well described by the nucleation rate expression proposed by Lothe & Pound (1962).

In this paper the condensation of ammonia, in mixture with an inert gas, during a supersonic expansion through a nozzle is examined. Oswatitsch (1941, 1942) produced the pioneering work on condensation phenomena. He formulated the general equations governing nozzle flows with a change of phase and discussed the necessary assumptions in detail. Wegener (1969) has made a complete review of previous work in this field.

We propose a new formulation for the mathematical description of the particle cloud and derive a system of differential equations for the calculation of the condensate mass fraction which govern quantities describing physically the particle size distribution.

#### MATHEMATICAL MODEL OF NON-EQUILIBRIUM CONDENSATION

Delhaye (1968), Marble (1963, 1970) and Mathieu (1975) among others have derived a general system of vectorial conservation equations for each of the phases of a two-phase flow with mass transfer.

In the description of the condensation process, the Knudsen number based on the particle size  $Kn_p = \lambda/2r$ , where  $\lambda$  is the mean free path of the gas molecules and  $r$  the size of the particle, plays the following dominant role: for very small or very large values of that number compared with unity, the gas flow around the particle corresponds respectively to the continuum or to the free molecular regime approximation. In a continuum, the mean velocity of the condensing molecules is the particle velocity. Indeed, the vapor molecules which are condensing on the particle surface diffuse through the gas around it. At the moment of their capture, the vapor molecules move with the velocity of the gas-particle interface. The total momentum transfer between the phases per unit volume of fluid is then

$$\mathbf{F}_p + \Gamma_p \mathbf{v}_p, \quad [1]$$

where  $\mathbf{F}_p$  is the force exerted by the gas on the particle cloud per unit volume of fluid,  $\Gamma_p$  the local rate of mass transfer of vapor from the gas to the particles per unit volume of fluid and  $\mathbf{v}_p$  is the barycentric velocity of the particle cloud. The total energy exchanged between gas and particles per unit volume of fluid is

$$\mathbf{F}_p \cdot \mathbf{v}_p + Q_p + \Gamma_p \left[ h_v(T_p) + \frac{1}{2} v_p^2 \right], \quad [2]$$

where  $Q_p$  is the heat quantity given up per unit time and unit volume of fluid by the gas to the particles,  $T_p$  is the mean temperature of the particle cloud and  $h_v$  is the vapor enthalpy per unit mass.

In a free molecular environment, the vapor molecules strike the particle surface practically without any mutual collisions. They are consequently captured in the gas dynamic and thermodynamic conditions. This capture only changes the terms associated with the mass transfer, which become

$$\Gamma_p \mathbf{v}_G \quad \text{and} \quad \Gamma_p \left[ h_v(T_G) + \frac{1}{2} v_G^2 \right] \quad [3]$$

where  $\mathbf{v}_G$  is the barycentric velocity of the gas and  $T_G$  its mean temperature.

In the approximation of the continuum, the conservation equations of mass, of momentum and of enthalpy for each phase may be written as

$$\frac{\partial \rho_G}{\partial t} + \text{div}(\rho_G \mathbf{v}_G) = -\Gamma_p, \quad [4]$$

$$\frac{\partial \rho_p}{\partial t} + \text{div}(\rho_p \mathbf{v}_p) = \Gamma_p, \quad [5]$$

where  $\rho_G$  and  $\rho_p$  are respectively the mass of gas and of condensed phase per unit volume of fluid;

$$\rho_G \frac{\partial \mathbf{v}_G}{\partial t} + \rho_G (\mathbf{v}_G \cdot \mathbf{grad}) \mathbf{v}_G = -\mathbf{grad} P + \mathbf{div} \underline{\underline{T}}_G^* - \mathbf{F}_p + \Gamma_p (\mathbf{v}_G - \mathbf{v}_p), \quad [6]$$

$$\rho_p \frac{\partial \mathbf{v}_p}{\partial t} + \rho_p (\mathbf{v}_p \cdot \mathbf{grad}) \mathbf{v}_p = \mathbf{F}_p, \quad [7]$$

where  $P$  is the pressure in the gas and  $\underline{\underline{T}}_G^*$  the viscous stress tensor in the gas;

$$\rho_G \frac{\partial h_G}{\partial t} + \rho_G \mathbf{v}_G \cdot \mathbf{grad} h_G = \frac{\partial P}{\partial t} + \mathbf{v}_G \cdot \mathbf{grad} P + \underline{\underline{T}}_G^* : \mathbf{grad} \mathbf{v}_G - \mathbf{div} \mathbf{q}_G + \mathbf{F}_p \cdot (\mathbf{v}_G - \mathbf{v}_p) - Q_p - \Gamma_p \left[ h_v(T_p) - h_G(T_G) + \frac{1}{2} |\mathbf{v}_G - \mathbf{v}_p|^2 \right], \quad [8]$$

$$\rho_p \frac{\partial h_p}{\partial t} + \rho_p \mathbf{v}_p \cdot \mathbf{grad} h_p = Q_p + \Gamma_p L(T_p), \quad [9]$$

where  $h_G$  and  $h_p$  are respectively the enthalpies of the gas and of the particle cloud per unit mass,  $\mathbf{q}_G$  the heat flux vector in the gas, and  $L$  the latent heat of condensation per unit mass.

In these balance equations, the mass, momentum and heat transfers between the phases may be expressed in the approximation of the continuum and in the Stokes' approximation, i.e.

$$Re_p = \frac{2\rho_G |\mathbf{v}_G - \mathbf{v}_p| r}{\mu_G} \leq 1, \quad [10]$$

where  $\mu_G$  is the dynamic viscosity of the gas, by the following expressions:

$$\Gamma_p = \frac{\rho_p}{\tau_D} \left[ \frac{P_v(T_G) - P_{\text{sat}}(T_p)}{P_v(T_G)} \right] \quad \text{with} \quad \tau_D = \frac{1}{3} \frac{\rho_s}{\rho_v} \frac{1}{D} r^2, \quad [11]$$

$\tau_D$  is the characteristic relaxation time associated with the mass-transfer process governed by the vapor diffusion through the gas,  $P_v$  and  $\rho_v$  are the partial pressure and the density of the vapor respectively,  $P_{\text{sat}}$  is the saturation pressure of the vapor at the particle surface,  $\rho_s$  is the density of the condensed phase and  $D$  is the binary diffusion coefficient of the vapor in the gas;

$$\mathbf{F}_p = \frac{\rho_p}{\tau_v} (\mathbf{v}_G - \mathbf{v}_p) \quad \text{with} \quad \tau_v = \frac{2}{9} \frac{\rho_s}{\mu_G} r^2, \quad [12]$$

$$Q_p = \frac{\rho_p}{\tau_T} C_s (T_G - T_p) \quad \text{with} \quad \tau_T = \frac{3}{2} Pr \frac{C_s}{C_{pG}} \tau_v, \quad [13]$$

$\tau_v$  and  $\tau_T$  are the characteristic relaxation times of velocity and temperature respectively,  $C_s$  and  $C_{pG}$  are the specific heats of the condensed phase and of the gas respectively and  $Pr$  is the gas Prandtl number ( $Pr = \mu_G C_{pG} / \lambda_G$  where  $\lambda_G$  is the gas thermal conductivity).

For high values of the Knudsen number  $Kn_p$ , the drag coefficient and the Nusselt number are corrected by expressions depending on  $Kn_p$  and given, among others, in the following references: Schaaf & Chambré (1958), Fuchs (1959, 1964), Gyarmathy (1962, 1974), Hidy & Brock (1970).

#### APPLICATION OF THE MATHEMATICAL MODEL OF CONDENSATION TO THE STUDY OF THE CONDENSATION ZONE IN A ONE-DIMENSIONAL FLOW

The condensation of a vapor of ammonia is examined in the supersonic part of a slowly divergent straight nozzle, under the usual assumptions proposed by Oswatitsch (1941) and specified by many authors, such as Wegener and his collaborators.

Wegener (1969), Wegener & Mack (1958), Wegener *et al.* (1972), among others, have shown that, under the conditions prevailing in supersonic nozzle expansions, the nucleation process is practically homogeneous provided that the concentrations in dust particles do not exceed about  $10^{12}$  particles/m<sup>3</sup>. Moreover, coalescence phenomena may be neglected for the typical particle concentrations in a condensation process.

The results of our computations show that, in the absence of particle coalescence, the condensation zone may be divided into two spatially separated zones:

(1) a narrow region, called the "nucleation zone", where the nuclei of critical size  $r^*$  appear at a rate  $J$ , mainly depending upon the prevailing supersaturation:  $S = P_v/P_{sat}$ ;

(2) a "growth zone", in which the probability of formation of new nuclei becomes negligible and where the critical nuclei grow by capture of molecules of the surrounding vapor at a rate depending upon the droplet growth law. The supersaturation  $S$  is the main quantity governing the condensation process, since the nucleation rate  $J$  and the critical size  $r^*$  strongly depend on it.

No significant appearance of the condensed phase is observed before a certain degree of supersaturation of the vapor is reached, for which the critical size  $r^*$  has become sufficiently small. As  $r^*$  is small, the value of  $J$  increases, giving rise to the rapid formation of a large number of nuclei. Then the supersaturation state collapses. This is due partly but not significantly to the decrease in the partial pressure of the vapor by depletion in the condensation process and mainly to the increase in the saturation pressure. The latter is due to the heating of the gas by the release of the latent heat of condensation. Then  $J$  falls very quickly and the nucleation zone ends. The formation of the condensed phase leads to deviations in the variations of flow quantities with respect to their isentropic variations. The jump in these quantities is initiated in the nucleation zone and develops afterwards in the growth zone until the two phases approach an equilibrium state.

#### STUDY OF THE NUCLEATION ZONE

The present status of theoretical and experimental knowledge does not suggest which of the classical expression or the Lothe & Pound (1969) expression is the more suitable one for the nucleation rate  $J$ .

The experimental results of Jaeger (1966), Kremmer & Okuromu (1963) and Jaeger *et al.* (1969) show that the theoretical results obtained for ammonia may agree with the experimental ones on the only condition that the Lothe & Pound (1969) expression for  $J$  is introduced into the mathematical formalism. However, this favorable conclusion as regards the validity of the Lothe & Pound (1969) expression of the homogeneous nucleation rate may perhaps be too optimistic. In fact, the agreement found is based on several assumptions regarding the experiments of Jaeger *et al.* (1969) and among them, the assumption that homogeneous nucleation, but neither binary nor heterogeneous nucleation occurred in the experiments. Hence, the equations are solved with the two expressions of  $J$  and the results obtained are compared.

It follows from the theory of homogeneous nucleation that the formation of nuclei under supersaturated conditions is due to fluctuations of the fluid density, that is to say from random collisions of vapor molecules and clusters. The number of critical size nuclei formed per unit time and unit volume in a stationary state is given by

$$J = \beta_v A Z C_0. \quad [14]$$

In [14],  $\beta_v$  is the collision frequency of vapor molecules on the unit surface of a cluster and is given from the kinetic theory of gases by

$$\beta_v = \frac{P_v}{\sqrt{2\pi m_v kT}}, \quad [15]$$

where  $m_v$  is the mass of a vapor molecule and  $k$  the Boltzmann constant.

$A(n^*)$  is the surface of a critical size nucleus and  $n^*$  the number of molecules in that nucleus.  $Z$  is known in the literature as the non-equilibrium factor of Zeldovich and is given by

$$Z = \frac{2}{A(n^*)} v_B \sqrt{\left(\frac{\sigma}{kT}\right)} \quad \text{with} \quad v_B = \mu_v / \rho_s N_0, \quad [16]$$

where  $\sigma$  is the surface tension,  $\mu_v$  is the vapor molecular weight and  $N_0$  the Avogadro's number.

The equilibrium concentration of critical size nuclei  $C_0(n^*)$  is given by

$$C_0(n^*) = c(1)_0 \exp[-\Delta G^*/kT], \quad [17]$$

where  $c(1)_0$  is the initial concentration of molecules and  $\Delta G^*$  is the maximum value of the free energy of formation of critical size nuclei.

It is expressed by

$$\Delta G^* = \frac{4\pi}{3} \sigma r^{*2}, \quad [18]$$

in which the critical size  $r^*$  is given by

$$r^* = \frac{2\sigma}{\rho_s R_v T \ln S}, \quad [19]$$

$R_v$  being the vapor constant.

For high expansion rates, the steady state nucleation rate  $J$  is not established immediately. It lags the thermodynamic conditions by a characteristic relaxation time  $t^*$ . The instationary expression for  $J$  is

$$J_t = J[1 - \exp(-t/t^*)]. \quad [20]$$

Feder *et al.* (1966) give for  $t^*$

$$1/t^* = 2\pi\xi\beta_v A(n^*)Z^2, \quad [21]$$

where  $\xi$  is the mass-accommodation coefficient.

For the flow conditions investigated here, the flow characteristic time is of the order of 25  $\mu$ s. For nuclei of 50  $\text{\AA}$  of an ammonia vapor, at the typical pressure of 0.1 atm. and a temperature of 200°K in the nucleation zone, the ratio of  $t^*$  to the flow characteristic time (for an arbitrary value of  $\xi$  equal to unity) is about  $4 \cdot 10^{-4}$ . Hence, the steady state approximation for  $J$  is fully justified.

In the expression for  $J$ , the factor which accounts for the nonisothermal character of the interactions between the gas molecules and the clusters in the process of dissipation of the latent heat of condensation from the nuclei has not been taken into account. Feder *et al.* (1966) and Lothe & Pound (1969) have shown that that term, which multiplies expression [14], does not change the value of  $J$  by more than an order of magnitude. Lothe & Pound (1969) have added statistical contributions to  $\Delta G^*$ , expressing the existence of translational and rotational degrees of freedom of the nuclei as rigid spheres. They have also added a term, called the partition function of replacement  $q_r$ , which accounts for the replacement of internal translational and torsional degrees of freedom of vibrations of the cluster in the bulk phase by translational and rotational degrees of freedom of the cluster in the gas phase.

The equilibrium concentration  $C_0(n^*)$  is then increased by a factor  $Q = q_{tr} \cdot q_{rot} / q_r$  in which  $q_{tr}$  and  $q_{rot}$  are the partition functions of translation and rotation respectively. Lothe & Pound (1969)

estimate a value of  $q_r$  of the order of  $10^3$  so that, under typical conditions in the nucleation zone for ammonia, factor  $Q$  reaches values of the order of  $10^{15}$ . However, some authors, Dunning (1969) for instance, have proposed values of  $q_r$  which restore an agreement between theoretical predictions and experimental results.

As a consequence of the disagreement on the value of  $q_r$ , among different authors, the following two expressions for  $J$  have been used in the present calculations

$$J_{\text{class}} = \left(\frac{P_v}{kT}\right)^2 \frac{1}{\rho_s} \left[\frac{2\sigma\mu_v}{\pi N_o}\right]^{1/2} \exp\left[-\frac{4\pi r^{*2}\sigma}{3kT}\right], \quad [22]$$

$$J_{L-P} = \frac{P_v}{\sqrt{(2\pi mkT)}} 2v_B \sqrt{\left(\frac{\sigma}{kT}\right) \frac{\sqrt{(\pi)}}{q_r^*} \left[\frac{2\pi n^* mkT}{h^2}\right]^{3/2}} \times \left[\frac{8\pi^2 I(n^*) kT}{h^2}\right]^{3/2} \exp\left[-\frac{4\pi r^{*2}\sigma}{3kT}\right]. \quad [23]$$

where  $h$  is the Planck constant and  $I(n^*)$  is the moment of inertia of the nucleus ( $I(n^*) = (2/5)n^*m_v r^{*2}$  for a sphere).

For a given temperature, these expressions are proportional to  $\exp[-K\sigma^3/(\ln S)^2]$ . Hence, they are very sensitive to macroscopic quantities like the surface tension  $\sigma$  and the latent heat of condensation, entering the expression of the saturation pressure in  $S$ . The values of these quantities must be extrapolated for small entities like clusters. For such small sizes, Tolman (1949) suggested a correction of the flat surface value  $\sigma_\infty$  given by

$$\sigma = \frac{\sigma_\infty}{1 + \delta/r}, \quad [24]$$

where  $\delta$  is a molecular length.

Wegener & Parlange (1967) have proposed a relation between the latent heat of condensation and the radius of curvature of the particle surface, which shows that the dependence becomes very weak for sizes higher than about 100 Å.

In the nucleation zone, the particles are so small (a few tens of Angströms) that there is practically no velocity slip with respect to the gas. Indeed, the velocity characteristic relaxation time  $\tau_v$  given by [12], is proportional to the square of the particle size. For instance, for a nucleus of 50 Å,  $\tau_v$  is about  $4 \cdot 10^{-9}$  s and for a size of 1000 Å, it is about  $10^{-7}$  s. Thus,  $\tau_v$  remains negligible with respect to the characteristic time of the flow (about 25  $\mu$ s) in the considered range of sizes. In another way, Wegener & Mack (1958) start from Newton's law relating the drag force and the particle acceleration in the Stokes' and in the continuum approximations. They calculate that, for water droplets and for typical gas viscosity, the particle sizes for which a slip velocity of 1% of the flow speed ( $v_G/v_p = 1.01$ ) is allowed are obtained by

$$r^2 \sim 10^{-9}/(dv_p/dx). \quad [25]$$

In the expansions considered here, a typical value of  $dv_p/dx$  is about  $10^5 \text{ s}^{-1}$  and the corresponding computed droplet size from [25] is  $10^{-7}$  m. As the computed Knudsen number  $Kn_p$  is of the order of 10, the calculation has to be made with free molecule values of the drag coefficient. In the conditions investigated here, the computed sizes are of the order of  $10^{-7}$  m too.

There is also practically no temperature difference between the phases since  $\tau_T$  is of the same order of magnitude as  $\tau_v$ . Moreover, for a mixture of a vapor and an inert gas, the latter favors the equalization of the phase temperatures. Indeed, in its interactions with the condensed phase, the inert gas plays the role of a heat sink. From the energy conservation for a particle established by Hill (1966) and Hill *et al.* (1963), expressing the balance between the different energy fluxes

associated with the mass fluxes of incident, reflected ratio and reemitted molecules, an approximate expression of the temperature  $T_p/T_G$  may be obtained. In that expression, the influence of the inert gas is described as follows: the ratio of the phase temperatures decreases when either the partial pressure ratio  $P_i/P_v$  or the molecular weight ratio  $\mu_v/\mu_i$  increases. That is physically explained by the fact that the latent heat of condensation released to the gas by absorption of vapor molecules into the nuclei is carried away due to the collisions of the gas molecules on the particle surfaces. The approximation of temperature equilibration between the phases is hence all the more accurate as the number of collisions of inert gas molecules between two collisions of vapor molecules on a nucleus is large.

The application of the mathematical model of condensation to a one-dimensional flow, for stationary conditions and in the approximation of the equality of the phase velocities and temperatures, leads to the following system of equations:

(1) Continuity equation

$$\rho u A = \dot{m} = \text{const.}, \quad [26]$$

where  $\rho (= \rho_G + \rho_p)$  is the density of the two-phase fluid,  $u (= v_G = v_p)$  is its velocity,  $A$  is the nozzle cross-section and  $\dot{m}$  the total mass flow rate.

(2) Equation of motion

$$\rho u \frac{du}{dx} = -\frac{dP}{dx}, \quad [27]$$

(3) energy equation

$$\frac{1}{2} u^2 + c_{po}(T - T_o) - X_p L = 0, \quad [28]$$

where  $T (= T_G = T_p)$  is the two-phase fluid temperature,  $T_o$  and  $c_{po}$  the temperature and the specific heat of the gas mixture in the stagnation chamber respectively and  $X_p$  the condensate mass fraction. The latter quantities are expressed as follows

$$c_{po} = (1 - X_{vo})c_{pi} + X_{vo}c_{pv}, \quad [29]$$

where  $X_{vo}$  is the vapor mass fraction in the stagnation chamber and  $c_{pi}$  and  $c_{pv}$  the specific heats of the inert gas and the vapor respectively;

$$X_p = \frac{\dot{m}_p}{\dot{m}}; \quad X_v = \frac{\dot{m}_v}{\dot{m}}; \quad \text{and} \quad X_p + X_v = X_{vo}, \quad [30]$$

where  $\dot{m}_p$  and  $\dot{m}_v$  are the local mass flow rates of the condensed phase and the vapor respectively.

To close the system of equations, a state equation is used and an expression for the condensate mass fraction  $X_p$  is established. The state equation for the gas is

$$P = \rho_G R \left[ \frac{1 - X_{vo}}{1 - X_p} \frac{1}{\mu_i} + \frac{X_{vo} - X_p}{1 - X_p} \frac{1}{\mu_v} \right] T, \quad [31]$$

where  $\mu_i$  and  $\mu_v$  are the molecular weights of the inert gas and the vapor respectively and  $R$  the universal gas constant. In this way, the five unknowns  $\rho$ ,  $u$ ,  $P$ ,  $T$  and  $X_p$  are obtained from five equations.

The physical process leading to the formation of the condensed phase at a point of observation located at a distance  $x$  of the nozzle throat allows the establishment of an expression for  $X_p$ . The

condensate mass observed at  $x$  is due, on the one hand to the creation of critical size nuclei in section  $x$  and on the other hand, to the growth of nuclei born in previous sections  $x'$  and observed at  $x$ .

The radius of the latter nuclei is given by

$$r(x, x') = r^*(x') + \int_{x'}^x \frac{dr}{d\xi} d\xi, \quad [32]$$

and their mass is

$$m(x, x') = \frac{4\pi}{3} \rho_s r^3(x, x'). \quad [33]$$

The number of particles nucleated per unit time in the elementary volume  $A(x') dx'$  about  $x'$  is:  $J(x')A(x') dx'$ . Hence, the mass fraction of condensed phase observed at  $x$  is

$$X_p(x) = \frac{4\pi\rho_s}{3\dot{m}} \int_{x_s}^x r^3(x, x') J(x') A(x') dx', \quad [34]$$

where  $x_s$  is a point at which the state of the vapor is the theoretical saturation one ( $J = 0$ ). In that expression,  $r(x, x')$  depends upon the whole history of the processes of creation and growth of the particles and is itself obtained by an integral in [32]. The numerical computation of  $X_p$  by [34] consists in following the evolutions of the particles formed at all the positions  $x'$  along their streamlines from  $x_s$  to  $x$ . For each position  $x$  of the computation, the values of the size  $r(x, x')$  at all the positions  $x'$  between  $x_s$  and  $x$  must be stored. That computational technique, although possible, is very cumbersome. Therefore, the integral in [34] is eliminated. A first differentiation of  $X_p(x)$  yields:

$$\frac{dX_p}{dx} = \frac{4\pi\rho_s}{3\dot{m}} \left\{ J(x)A(x)r^{*3}(x) + 3 \int_{x_s}^x r^2(x, x') \frac{dr(x, x')}{dx} J(x')A(x') dx' \right\} \quad [35]$$

The physical meaning of that expression is clear: the first term represents the condensate mass appearing by nucleation in section  $x$  and the second one represents the condensate mass due to the growth of particles previously formed in sections  $x'$  ( $x_s \leq x' \leq x$ ).

Equation [35] still contains an integral and the particle growth law. In the conditions investigated here, the gas mean free path varies typically between  $10^{-7}$  and  $10^{-6}$  m and the mean size of the particles from 100 to 1000 Å. The Knudsen number  $Kn_p$  is thus of the order of 10. Hence, the gas flows around a particle in the free molecular regime. From the kinetic theory of gases, a particle growth law may then be obtained from the balance of two opposite molecular fluxes; one obtains

$$\frac{dr}{dt} = u \frac{dr}{dx} = \xi \frac{1}{\rho_s \sqrt{(2\pi R_v)}} \left[ \frac{P_v}{\sqrt{(T_G)}} - \frac{P_D}{\sqrt{(T_p)}} \right], \quad [36]$$

where  $P_D$  is the saturation pressure of the vapor at the particle surface. It is given by the Helmholtz equation as

$$P_D(T_p) = P_\infty(T_p) \exp [2\sigma/(\rho_s R_v T_p r)], \quad [37]$$

where  $P_\infty$  is the theoretical saturation pressure given by the Clausius–Clapeyron relation, i.e.

$$P_\infty(T_p) = P_o \exp \left[ \frac{L}{R_v T_o} \left( 1 - \frac{T_o}{T_p} \right) \right], \quad [38]$$



in which  $P_o$  and  $T_o$  represent a reference state on the theoretical saturation curve.

In a free molecular environment,  $(dr/dt)$  does not depend any longer upon the particle radius  $r(x, x')$  for sizes larger than about  $50 \text{ \AA}$ , since  $P_D/P_\infty$  is then about equal to unity. As larger sizes are rapidly reached in the nucleation zone, the growth law acts practically in the same way on all particles independently of their size during most of the condensation process.

As  $dr/dx$  does not depend on  $r$ , it no longer depends on the condensation history. Hence it is no longer a function of  $x'$  but only of  $x$ . Therefore it may come out of the integral in [35].

After four differentiations of the different integrals, [35] is then replaced by the following four differential equations

$$\frac{dF_i}{dx} = JA r^{*i} + i \frac{dr}{dx} F_{i-1} (i = 0, 1, 2, 3). \quad [39]$$

The quantities  $F_i$  are the moments of the size distribution of all the particles observed at  $x$  and are given by

$$F_i = \int_{x_s}^x r^i(x, x') J(x') A(x') dx' (i = 0, 1, 2, 3). \quad [40]$$

The condensate mass fraction is then obtained by

$$X_p = \frac{4\pi}{3\bar{m}} \rho_s F_3.$$

Although the knowledge of the quantities  $F_i$  does not allow a plotting of the size distribution curve observed at a position  $x$ , it gives quantitative indications about that distribution.

The total number of particles observed at the position  $x$  per unit time is

$$Z_o \equiv F_o. \quad [41]$$

The mean size is given by:

$$Z_1 \equiv \bar{r} = F_1/F_o. \quad [42]$$

The second and third centered relative moments, quantifying the dispersion and the distortion of the distribution respectively, are expressed by

$$Z_2 \equiv \overline{(r - \bar{r})^2} = \bar{r}^2 - (\bar{r})^2 = \frac{F_2}{F_o} - \left(\frac{F_1}{F_o}\right)^2, \quad [43]$$

and

$$Z_3 \equiv \overline{(r - \bar{r})^3} = \bar{r}^3 - 3\bar{r}^2\bar{r} + 2(\bar{r})^3 = \frac{F_3}{F_o} - 3\frac{F_1}{F_o} \cdot \frac{F_2}{F_o} + 2\left(\frac{F_1}{F_o}\right)^3, \quad [44]$$

with

$$\bar{r}^i = \frac{\int_{x_s}^x r^i(x, x') J(x') A(x') dx'}{\int_{x_s}^x J(x') A(x') dx'} = \frac{F_i}{F_o} (i = 1, 2, 3). \quad [45]$$

After some algebraic manipulations, [35] is replaced by the following four differential equations

$$\frac{dZ_0}{dx} = JA, \quad [46]$$

$$\frac{dZ_1}{dx} = \frac{JA}{Z_0} (r^* - Z_1) + \frac{dr}{dx}, \quad [47]$$

$$\frac{dZ_2}{dx} = \frac{JA}{Z_0} [(r^* - Z_1)^2 - Z_2], \quad [48]$$

$$\frac{dZ_3}{dx} = \frac{JA}{Z_0} [(r^* - Z_1)^3 - 3(r^* - Z_1)Z_2 - Z_3]. \quad [49]$$

For the numerical treatment of these equations by the Runge–Kutta–Gill method, the following initial conditions for the quantities  $Z$  are used

$$Z_i(o) = 0 \quad \text{at the nozzle throat } x = o \quad (i = 0, 1, 2, 3).$$

The condensate mass fraction is then obtained by

$$X_p = \frac{4\pi\rho_s}{3\dot{m}} Z_0[Z_3 + 3Z_1Z_2 + (Z_1)^3]. \quad [50]$$

The treatment of the system [46]–[49] instead of [35] for  $X_p$  allows avoidance of the numerical computation of an integral along the particle streamlines, as Chmielewski & Sherman (1970) have done. Thanks to that treatment we achieve a substantial economy of the occupation of the computer memory and a reduction of computational time.

The four quantities  $Z$  and their evolutions already give a good idea of the shape of the particle size distribution and its evolution. However, the size distribution curves shown in figure 3 are generated by a numerical step by step procedure. At each new step,  $x + \Delta x$ , the curve is shifted due

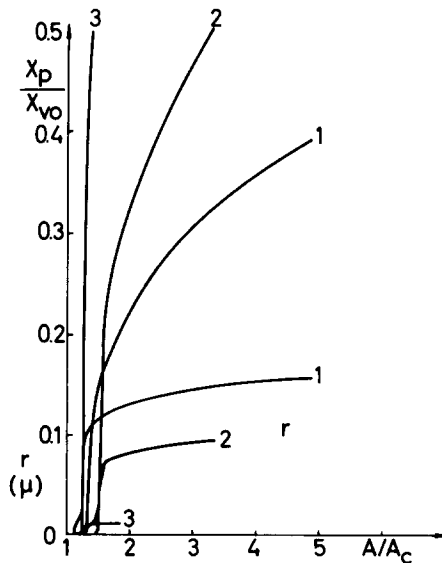


Figure 1. Distributions of the reduced mass-fraction  $X_p/X_{v0}$  and of the surface-averaged mean size ( $\bar{r}^2 = F_2/F_0$  in micron) of nuclei of the condensed phase of a  $\text{NH}_3$  vapor in function of the reduced area  $A/A_c$ . Curve 1:  $X_{v0} = 0.2$ ; inert gas = air;  $J = J_{L-p}$ , [23]. Curve 2:  $X_{v0} = 0.1$ ; inert gas = air;  $J = J_{L-p}$ , [23]. Curve 3:  $X_{v0} = 0.2$ ; inert gas = helium;  $J = J_{L-p}$ , [23]. The other parameters, kept constant, are:  $P_0 = 2$  atm;  $T_0 = 265^\circ\text{K}$ ; mass-accommodation coefficient:  $\xi = 1$ ; half-angle of the divergent of a two-dimensional straight nozzle:  $4^\circ$ ; throat area:  $A_c = 2 \cdot 10^{-5}$  m<sup>2</sup>; throat height:  $h = 38 \cdot 10^{-4}$  m;  $\sigma/\sigma_\infty = 1$ .

to the growth of the particles existing at  $x$  and arriving at  $x + \Delta x$ . They are all growing in the same way since the growth law [36] is independent of the particle size. Hence, the change of shape of the curves in the nucleation zone is only due to the addition to the distribution of the new nuclei formed at critical size at  $x + \Delta x$ . The shape and the evolution of the size distribution curve in the nucleation zone are physically explained from the evolutions of the nucleation rate  $J$  and the critical size  $r^*$ . Indeed, the gradients of quantities  $Z$  contain expressions proportional to  $J$  and depending on  $r^*$ . The quantities  $J$  and  $r^*$  vary in opposite sense (see figure 2) and reach their extrema at the same point in the nozzle. At the beginning of the nucleation process, the first nuclei are formed at a size  $r^*$  and in number  $J$  per unit time and unit volume, both determined by the value of the local supersaturation  $S$ . As the point of observation moves downstream in the nozzle, the supersaturation increases and new nuclei are created at a smaller size  $r^*$  and in a higher number  $J$ . The particle size distribution curves (1–5 in figure 3) are built up in that way. As long as  $J$  and  $r^*$  have not both reached their extrema, these curves evolve due to the particle growth which increases the size of all the particles with the same amount and leads to a variation of the mean size as shown by [47]. As soon as the point of observation proceeds beyond the position of the maximum value of  $J$ , the nuclei are formed in a smaller number  $J$  and at a higher size  $r^*$ . But the increase in  $r^*$  is smaller than the increase in size of the preexisting nuclei by growth so that the distribution curve exhibits a maximum (like curves 6–9). As  $J$  becomes negligible, no new nuclei are created and the particles all grow in the same way since the growth law is independent of the size. Consequently, the size distribution curve translates, without change of shape, along the size axis (curves 8 and 9).

STUDY OF THE GROWTH ZONE

As the rate of condensate mass production by formation of critical size nuclei becomes negligible with respect to the rate of condensation by growth of the existing nuclei, the values of  $J$  become negligible compared to its maximum value. The supersaturation state collapses and the nucleation zone ends.

The computational results show that the mean size of the particles does not exceed one micron.

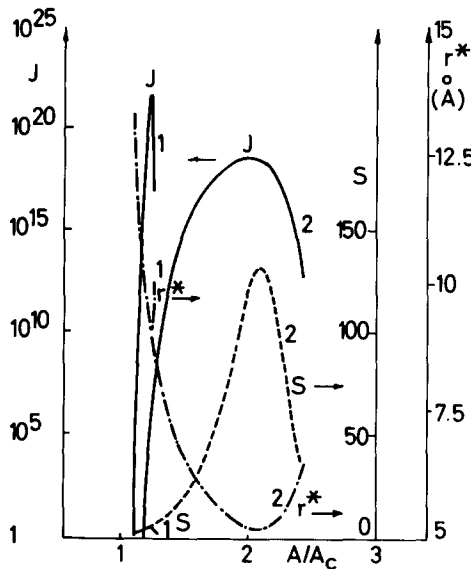


Figure 2. Variations of the nucleation rate  $J(m^{-3} \cdot s^{-1})$ , of the supersaturation  $S$  and of the critical size  $r^*$  (in Å) with  $A/A_c$  in the nucleation zone for an ammonia-air mixture. Curve 1:  $X_{v_0} = 0.2$ ; inert gas = air;  $J = J_{L-P}$ , [23]. Curve 2:  $X_{v_0} = 0.2$ ; inert gas = air;  $J = J_{class}$ , [22]. The other parameters, kept constant, are the same as in the caption of figure 1. The classical and the semi-statistical  $J_{L-P}$  expressions of  $J$  are related as follows:

$$J_{L-P} = 3.66 \cdot 10^5 \frac{\rho_s^3}{P_v} (kT)^4 \frac{r^{*12}}{h^6} \frac{1}{q_r} J_{class}$$

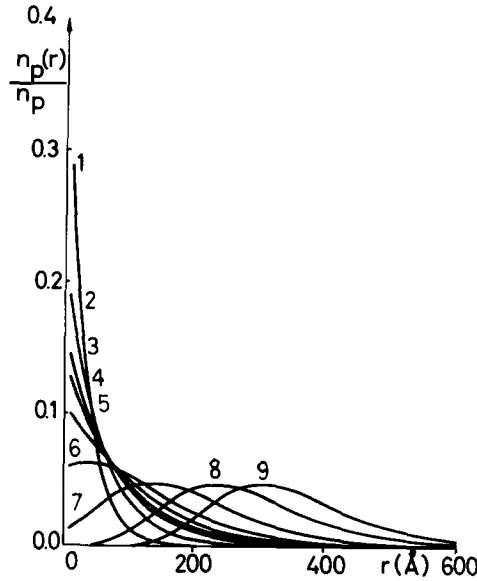


Figure 3. Distribution of the reduced particle number per unit volume  $n_p(r)/n_p$ , with  $n_p = \int_0^\infty n_p(r) dr$ , of  $\text{NH}_3$  particles in function of their surface-averaged mean size  $r = (F_2/F_0)^{1/2}$  in  $\text{Å}$  at various locations in the condensation zone.

Curve	1	2	3	4	5	6	7	8	9
$A/A_c$	1.14	1.19	1.225	1.24	1.25	1.255	1.26	1.27	1.28
$x$ (mm) (distance from throat)	3.84	5.42	6.21	6.71	6.9	7.10	7.23	7.5	7.68

From [25], the no slip condition is still a good approximation. For such sizes, the thermal equilibrium condition remains valid too.

In the growth zone, the values of  $J$  become negligible. The system [46]–[49] becomes

$$Z_0 \equiv F_0 = \text{const.}, \tag{51}$$

$$\frac{dZ_1}{dx} \equiv \frac{d\bar{r}}{dx} = \frac{dr}{dx}, \tag{52}$$

$$Z_2 \equiv \overline{(r - \bar{r})^2} = \text{const.}, \tag{53}$$

$$Z_3 \equiv \overline{(r - \bar{r})^3} = \text{const.} \tag{54}$$

As  $Z_0$ ,  $Z_2$  and  $Z_3$  have been computed at the end of the nucleation zone, they are known everywhere in the growth zone since they are conserved.

That system has a physical meaning. As no new nuclei are created in the growth zone, the number of particles passing at a position  $x$  per unit time remains constant. As the particle size distribution function moves along the size axis without any change of shape, all the moments are conserved in that translation. In particular  $Z_2$  and  $Z_3$ , characterizing the dispersion and the distortion of the distribution, remain constant. Moreover, the curve is shifted due to the variation of the mean size  $\bar{r}$  which is the same as the variation of the individual sizes  $r$ .

The advantage of this new formulation of the differential equations describing the particle cloud is essentially of a numerical nature. Indeed, the system [46–49] leading to the computation of the condensate mass fraction in the nucleation zone becomes a system of only one differential equation and three algebraic equations in the growth zone. These latter give the quantities  $Z_0$ ,  $Z_2$  and  $Z_3$  exactly and make programming easier. Hence, that formulation leads to an increase in the numerical precision and to a reduction of the computational time. As it is used in the largest part of the condensation zone, it also leads to a significant reduction in the computational cost.

## ANALYSIS OF THE RESULTS AND CONCLUSIONS

The influence of the presence of an inert gas on the condensation process of a vapor is analyzed. The numerical results show that an increase of the mass fraction  $X_i$  of the inert gas in the nozzle reservoir leads to a shift of the onset point of measurable condensation downstream from the nozzle throat. This may be physically explained by a decrease of the velocity of the gaseous mixture ammonia-air before the onset of condensation. Indeed, as  $\mu_i$  is larger than  $\mu_v$ , an increase of  $X_i$  results in an increase of the mean molecular mass  $\bar{\mu}$  of the gaseous mixture at a given nozzle position and accordingly in a decrease of its velocity. It follows that the thermodynamic conditions of condensation (Wilson point) are reached farther downstream in the expansion. Moreover, an increase of  $X_i$  for the ammonia-air mixture results in an enlargement of the nucleation zone.

If the inert gas is helium, an increase of  $X_i$ , resulting in a decrease of  $\bar{\mu}$  ( $\mu_i$  being smaller than  $\mu_v$ ), gives rise to an increase of the expansion rate. It follows that a shift of the onset point of condensation towards the nozzle throat occurs.

Figure 1 shows that the inert gas is really a sink for the latent heat of condensation. An increase of  $X_i$  for a given inert gas results in an increase of the condensation rate (see curves 1 and 2 for  $X_p/X_{vo}$ ). For a given  $X_i$ , the condensate mass production rate increases faster for helium whose specific heat is larger than for air (see curves 1 and 3). As  $X_i$  increases, the particles have a smaller size. That effect is still more marked as the inert gas is helium.

The computational results show that an increase of  $X_i$  for the ammonia-air mixture results in a softening of the condensation peak. For an increase of  $X_i$  from 0 (pure vapor) to higher values, the condensation peak, at first well marked, softens, flattens and finally disappears. These phenomena are explained from the expression of the pressure gradient deduced from [26]–[31], i.e.

$$\frac{1}{P} \frac{dP}{dx} = \frac{-\frac{1}{A} \frac{dA}{dx} + \frac{1}{1-X_p} \left[ \eta \frac{L}{\bar{c}_p T} - \frac{\bar{\mu}}{\mu_v} \right] \frac{dX_p}{dx}}{1 - (1-X_p) \frac{1}{\gamma M^2} - \eta \frac{\bar{R}}{\bar{c}_p}},$$

with

$$M^2 = a^2/u^2 = \gamma \bar{R} T / u^2, \quad \bar{R} = R / \bar{\mu}, \quad \bar{c}_p = c_{p0} + X_p (c_s - c_{pv})$$

and with

$$\eta = \frac{1}{1 + \frac{X_p c_s}{1 - X_p \bar{c}_p}},$$

where  $\gamma$  is the specific heat ratio of the gas mixture and  $M$  the frozen Mach number. The pressure distribution essentially depends on two terms: the effect of the nozzle geometry and the effect of the phase change. In a supersonic flow ( $M > 1$ ), as the effect of the change of phase dominates the nozzle expansion rate, a pressure jump is observed (see figure 4). In the opposite case, the pressure decreases monotonically everywhere. When the two effects have values of the same order, the peak disappears and the pressure profile exhibits a flat section.

From figure 2 it is evident that the nucleation zone obtained by the use of the Lothe & Pound (1969) expression of  $J$  [23] is quite different from that obtained with the classical expression [22]. The onset point of condensation moves downstream and the nucleation zone is wider when the classical  $J$  is used. The numerical results show that the deviations of the pressure, temperature and velocity distributions from the isentropes are smaller and that the condensation rate is slower with the use of the classical  $J$ .

Figure 4 shows a comparison of computed results for ammonia in mixture with air with Jaeger's experimental data (1969). There is a generally close agreement between theoretical and

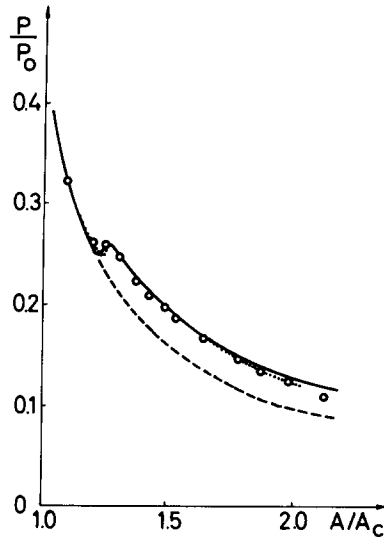


Figure 4. Reduced pressure profiles in function of the reduced area  $A/A_c$  for condensation of ammonia in mixture with air in Jaeger's two-dimensional straight nozzle (nozzle II in reference: Jaeger *et al.* 1969). Dashed line: isentropic expansion, Dotted line: theoretical profile computed by Jaeger, Continuous line: theoretical profile computed in the present work, Circles: experimental data of Jaeger *et al.* (1969). The different parameters are:  $P_o = 4.054$  atm.;  $T_o = 283.7^\circ\text{K}$ ;  $Xv_o = 0.169$ ; inert gas = air;  $\xi = 1$ ;  $\sigma/\sigma_w = 1$ ;  $J = J_{L-P}$  [23].

experimental results. Our numerical results disagree with those of Jaeger (1969) in the region of the onset point of condensation. The discrepancy in the pressure distributions in the nucleation zone is mainly due to uncertainties in the value of certain quantities like the replacement partition function, the surface tension, the saturation pressure and the mass- and thermal-accommodation coefficients.

In conclusion, our new formulation of the differential equations describing the particle cloud is physically closely related to the size distribution and leads to some substantial numerical advantages, principally in the growth zone. The validity of the mathematical model developed in this paper has been tested by comparison of theoretical predictions with experimental data and has been found satisfactory.

*Acknowledgements*—Fruitful discussions with Professor J. J. Smolderen (U.Lg.), director of the von Karman Institute for Fluid Dynamics in Belgium, are gratefully acknowledged. We thank Professor M. Giot (U.C.L.) for his helpful comments, and Professor G. Burnay (U.Lg.) for trusting us with a theoretical research about an aerodynamic process of uranium isotopes separation.

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