

Condensation of water vapour during supersonic expansion in nozzles

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Existing data on the condensation of steam and moist air in supersonic nozzles are compared with predictions based on nucleation and drop-growth theory. It is concluded that, if the surface tension is assumed independent of curvature, and the classical liquid-drop theory (based on a stationary liquid drop) is used, the theory is in general agreement with the data. The effects of uncertainties in cluster surface energy and also of the large corrections to nucleation theory due to the 'gasification' concept are examined. The gasification correction is in accord with experimental data only if the surface tension is considered to rise significantly with curvature. In neither case can the Tolman or Kirkwood–Buff equations be supported. A review of existing data shows that there is some question as to the appropriate value of the condensation coefficient but this is of little consequence as long as the accommodation coefficient for the liquid–vapour surface is taken to be unity. The usefulness of the nozzle experiments for testing the validity of nucleation theory is demonstrated.

1. Introduction

1.1. *Condensation in supersonic nozzles*

The qualitative effects of condensation in nozzle flows are quite well known and have been described in detail by Wegener & Mack (1958) in a comprehensive review paper. For most vapours there is a wide range of stagnation states from which an expansion isentrope will intersect the vapour–liquid coexistence line. Expansion in supersonic nozzles is typically so very rapid that the fluid departs radically from the equilibrium phase distribution. Water vapour will readily expand to a supersaturation (the ratio of actual vapour pressure to the equilibrium saturation value corresponding to the local temperature) of six or eight before any of the liquid phase appears. Mercury vapour has been known to expand to a supersaturation of 2000 without condensing.

The transition between supersaturation and equilibrium conditions may be very abrupt, e.g. the condensation 'shock', or spread out over a considerable region of space, depending on the density and speed of the flow.

The two principal effects of condensation on the flow as a whole are the removal of a portion of the vapour phase and the 'heating' of the remainder to absorb the energy extracted from the condensed phase. In the usual case, the ratio $h_{fg}/C_P T$ (h_{fg} being the enthalpy change during condensation, C_P being the specific heat

and T the local temperature) is greater than unity and this means that 'heating' has a larger effect on the stream properties than the vapour removal. Consequently the effects of condensation are like those of heat addition; in supersonic flow the stream pressure and temperature tend to rise.

The condensate formed in nozzle flows is in the form of very small particles, usually less than 1000 Å in size, so that except in a shock zone velocity 'slip' between vapour and liquid phases is usually negligible.

The mechanism for the liquid-phase formation is generally the spontaneous formation (homogeneous nucleation) of liquid nuclei from the pure vapour at a sufficiently high supersaturation. In high-speed nozzle flows, the time scale is far too short for any credible quantity of reasonably sized dust particles to provide significant surface area for the vapour to condense upon. Even if 10 % of the flow were composed of 0.1 micron dust particles, homogeneous nucleation might play the dominant role in providing condensation sites. Heterogeneous condensation can become significant if there is a plentiful supply of ions, or if the vapour carries within it a small quantity of another vapour which has condensed at a higher pressure and temperature; this preceding condensation may provide a sufficient number of small nuclei, in the size range 10 Å to 100 Å, to permit subsequent condensation of the carrier without significant supersaturation. Usually, however, nozzle flow condensation implies a homogeneous nucleation mechanism.

1.2. *Uncertainties in nucleation theory*

The liquid-drop theory of homogeneous nucleation (see, for example, Frenkel 1946), which for some time has been thought to be in reasonable accord with cloud-chamber data on water vapour, has been under increasing theoretical attack in recent years. Lothe & Pound (1962) and others have emphasized that important terms were generally omitted in derivation of the nucleation-rate equation. By taking into account the free energies of translation and rotation of the condensation cluster, Lothe & Pound have argued that the rate equation should be multiplied by a factor whose typical magnitude (for H₂O) is 10¹⁷. Courtney (1965), following Kuhrt (1952), has also taken these quantities into account but obtains for H₂O a factor of 10⁹ instead. These corrections, which result from considering the condensate particles to act as large molecules, are referred to in the following as 'gasification' factors.

A very important term in the estimation of nucleation rate is the surface energy of the condensation nuclei, which are so small (10–100 atoms) that their surface tensions might differ significantly from the flat-film value. Unfortunately several studies of the dependence of surface tension on curvature (see, for example, Stever 1958; Oriani & Sundquist 1963) have failed to provide agreement on even the sign of the correction. The Kirkwood–Buff equation relates the surface tension to the radius of curvature as follows:

$$\frac{\sigma}{\sigma_{\infty}} = \frac{1}{1 + \delta/r},$$

in which σ_{∞} is the surface tension of an infinite flat-film and δ is of the order of one molecular diameter. Since, for typical nuclei, r is perhaps only 3 or 4 times δ , this

formula predicts a rather large reduction of surface tension. On the other hand, Oriani & Sundquist have predicted that the surface tension of nuclei containing 10–100 atoms should be about 25 % larger than the flat-film value. This degree of discrepancy in theoretical predictions means a very large uncertainty in predicting nucleation rate.

There is thus a great need for reliable experimental data to help resolve some of these problems. Cloud-chamber data have been reviewed by Oriani & Sundquist (1963), but these data are not easy to interpret and show considerable scatter. It is the purpose of this paper to compare the results of nucleation theory with data on condensation of water vapour in steam and air nozzles. It is found that the data are clearly in much better agreement with the Frenkel–Zeldovich equation than with the Lothe–Pound results. However, firm conclusions cannot be drawn because of the uncertainty of the surface energy. Satisfactory experimental evaluation of the validity of a nucleation-rate equation must include accurate data on substances other than H₂O.

1.3. *Cloud-chamber measurements*

Experimental data from cloud chambers have often been used in discussions of the validity of nucleation theory. Oriani & Sundquist (1963), for example, have recently compared experimental results from Sander & Damkoehler (1943), Pound, Madonna & Sciulli (1955), Powell (1928), Wilson (1900) and Clark & Rodebush (1953). (They conclude that the nucleation equation, modified as mentioned earlier to include the results of ‘gasification’, and using their surface-energy correction, is in substantial agreement with these experimental results.) However, as Barnard (1953) has clearly pointed out (and as the experimental scatter shown by Oriani & Sundquist attests) the interpretation of cloud-chamber data is itself an uncertain process. It has generally been assumed that the appearance of a cloud corresponds to a rate of 1 nucleus/sec cm³ (though some observers look for a denser cloud than others). Barnard argues, however, that the actual rate corresponding to the appearance of the clouds could easily be from 10² to 10⁸ nuclei/sec cm³. Moreover, it is not entirely clear what role wall heat transfer has played in certain small-scale experiments. Further, the experiment is essentially unsteady and the limiting supersaturation observed will depend on the expansion time scale.

1.4. *Nozzle measurements*

In view of the above-mentioned difficulties in interpreting cloud-chamber data, and of the considerable quantity of data reported on the effects of condensation in nozzles, it seems somewhat surprising that more attention has not been paid to nozzle experiments in evaluating the validity of nucleation theory. The relative advantages of the nozzle experiment are that it is in steady state; the effects of condensation may be marked by pressure measurements rather than the appearance of a cloud of arbitrary density; the whole history of the expansion is easily obtained; the effects of condensation are easily derived from a one-dimensional frictionless gas-dynamic model, which is a very good approximation in most experiments (considering that part of the flow outside of the boundary layers);

it has been shown by Stodola (1927) and others that for this type of expansion the effects of dust particles are entirely insignificant so that homogeneous nucleation obtains. In a typical expansion of steam 10^{15} nuclei/cm³ are spontaneously formed whereas a maximum credible concentration of dust particles might be 10^8 /cm³. (An exception to this is the condensation of a multi-constituent fluid such as air in which the prior condensation of CO₂ may produce sufficient nuclei to remove the possibility of supersaturation and homogeneous nucleation of N₂ upon continued expansion.)

In the past decades considerable data have been accumulated on the effects of steam condensation in nozzles (e.g. Yellot 1934; Yellot & Holland 1937; Rettaliata 1936; Binnie & Woods 1938; Binnie & Green 1942; Gyarmathy & Meyer 1965). The only detailed comparison of these data with nucleation theory appears to have been done by Oswatitsch (1942), who used the Becker & Döring (1935) equation with a suitable drop-growth equation to predict the measured pressure distributions in the nozzle. Although the hand computation he used was very laborious, he was at least able to establish from a limited number of data the qualitative validity of the theory.

Experimental data on condensation of water vapour in air nozzles have been reported by Wegener & Pouring (1964) and others (see Wegener & Mack 1958 and Stever 1958 for reviews of various results).

Although light-scattering measurements can in principle be used to determine drop sizes in condensing streams, the feasibility of this kind of measurement has yet to be fully established. However, much can be learned about the kinetics of a condensation process from its effect on the pressure distribution of a supersonic stream. To interpret experimental results it is necessary to calculate the growth rate of condensed clusters and also the effect of the growth process on the dynamics of the expanding stream, but these two steps are not difficult. The size of the growing cluster is generally less than the mean free path so that the fluxes of mass and energy to and from its surface can be easily estimated. Since the drops are so small, the gas-dynamic effects are also easily determined.

In summary, a considerable quantity of data is available on the condensation of water vapour in supersonic nozzles. Apart from the limited hand calculations reported by Oswatitsch little has been done to compare these experimental results with the predictions of nucleation theory. On no other fluid do we have such extensive data and, as suggested already, nozzle data may be more useful than corresponding information from cloud chambers. It is the purpose of this paper to effect such a comparison between theory and experiment. The work has assumed greater urgency in the past few years on various grounds. There is increasing need for methods which will predict the condensation of a variety of fluids. At the same time recent theoretical work has emphasized considerable uncertainties which are not yet resolved.

2. Nucleation

Various methods of deriving the classical drop nucleation equation (the drop or cluster being assumed stationary in space) yield results of the following form:

$$I = c\dot{n}(4\pi r^*{}^2)n \exp(-\Delta G^*/kT), \quad (1)$$

in which I is the nucleation rate, per unit volume, per unit time, c a factor varying by one or two orders of magnitude depending on particular approximations used in deriving the equation, \dot{n} the number of particles impinging on unit surface per unit time (from kinetic theory, $\dot{n} = P/(2\pi nkT)^{1/2}$), r^* the critical nucleus size, n the concentration of vapour molecules, ΔG^* the free energy of formation of a critical-sized nucleus.

Until recently the free energy of formation of the critical nucleus ΔG^* was usually evaluated by assuming it to be the sum of three terms:

(i) the change in free energy of the vapour molecules in reducing their pressure from P to the flat-film saturation value P_∞ (all at temperature T)

$$\Delta G_1^* = -g^*kT \ln(P/P_\infty);$$

in which g^* is the number of molecules in the critical-sized nucleus;

(ii) the change in free energy during transition from vapour to a flat liquid film at pressure P_∞ and temperature T ,

$$\Delta G_2^* = 0;$$

(iii) the surface free energy necessary for creation of small liquid drops

$$\Delta G_3^* = 4\pi(r^*)^2\sigma,$$

in which σ is the surface tension.

Summing these contributions gives

$$\Delta G^* = 4\pi(r^*)^2\sigma - g^*kT \ln(P/P_\infty).$$

This function has a maximum of

$$\Delta G^* = \frac{4}{3}\pi(r^*)^2\sigma. \quad (2)$$

at a size (the 'critical' size r^*) given by

$$r^* = \frac{2\sigma v}{kT \ln(P/P_\infty)} = \frac{2\sigma}{\rho_L RT \ln(P/P_\infty)},$$

in which v is the volume per molecule in the liquid, and ρ_L is the liquid density. It is the existence of this maximum that gives rise to the notion of a critical-sized nucleus; this is the nucleus which is the most difficult to form. It may be shown that the equilibrium concentration of these critical-sized nuclei would be

$$n_{\text{equilibrium}}^* = n \exp(-\Delta G^*/kT).$$

Taking the simplest possible view, the earliest derivations assumed that the nucleation rate was proportional to this equilibrium concentration times the rate of impingement of particles on the surface of critical-sized nuclei. This, which corresponds to $c = 1$ in equation (1), is the rate at which critical-sized nuclei are converted to clusters containing $g^* + 1$ molecules.

In later treatments account was taken of the fact that the equilibrium spoken of above is unstable and therefore purely hypothetical. Also it was recognized that evaporation and condensation take place simultaneously as the cluster grows. It was to satisfy the first objection that the concept of a steady-state

nucleation process was introduced in which a non-equilibrium but steady-state distribution of cluster sizes up through the critical cluster size was postulated. The process of nucleation is considered to be the flow of a constant net current of nuclei through a steady distribution of nucleus sizes. That is, the net rate at which g -sized nuclei grow to $(g + 1)$ -sized nuclei is just equal to the net rate at which g -sized nuclei grow from $(g - 1)$ -sized ones, so that the concentration of nuclei of size g is constant. Nuclei cease to be considered part of the distribution when they are much bigger than the critical size, and the supply of vapour molecules is regarded as infinite. With this simplifying concept it has been shown how the steady-state cluster distribution and the nucleation rate may easily be derived (see Frenkel 1946).

Frenkel's result is

$$I = (p/kT)^2 v \sqrt{(2\sigma/\pi m)} \exp\{-4\pi\sigma(r^*)^2/3kT\}, \quad (3)$$

which corresponds to

$$c = \left[\frac{\ln P/P_\infty}{6\pi g^*} \right]^{\frac{1}{2}}$$

in equation (1).

For $P/P_\infty = 6$ and $g^* = 60$, $c = 0.04$, so that these improvements result in a reduction of two orders of magnitude in the nucleation rate. As will be shown later, two-orders-of-magnitude change in nucleation rate will not have a large effect on the gas dynamics in a nozzle in which condensation is occurring.

Method	P/P_∞
Becker-Döring (1935)	5.28
Volmer (1939), Frenkel (1946)	5.10
Sander-Damkoehler (1943)	4.44
Barnard (1953)	4.72
Yang (1963)	4.63

TABLE 1. Supersaturation for a nucleation rate of $1 \text{ cm}^{-3} \text{ sec}^{-1}$

The question of whether the steady-state model of condensation is realistic has received attention by a number of authors (e.g. Probstein 1951; Courtney 1962*a, b*; Feder, Russell, Lothe & Pound 1965). It now seems fairly clear that the time necessary to reach steady state would be of the order of a few micro-seconds for water (except perhaps at very low temperatures). This time is one or two orders of magnitude less than the time for the fluid to flow through the nucleation zone in most nozzles so we can feel fairly confident that the steady-state-nucleation equation is reasonable.

Numerical comparisons of the 'critical' supersaturation (i.e. the supersaturation corresponding to $I = 1 \text{ cm}^{-3} \text{ sec}^{-1}$) show that the results of numerous authors on deriving the classical nucleation are not greatly different. Yang (1963), for example, has compared the equation obtained by Barnard (1953), Becker & Döring (1935), Volmer (1939), and Sander & Damkoehler (1943). Yang has shown that the equations of Frenkel (1946) and Zeldovich (1942) are identical with the one obtained by Volmer. Also he has calculated the supersaturation required for

a nucleation rate of $1 \text{ cm}^{-3} \text{ sec}^{-1}$ at $261.0 \text{ }^\circ\text{K}$ using various methods. The results are given in table 1. Considering the accuracy to which the nucleation rate must be known in order to predict the effects of condensation on the nozzle gas dynamics, these are not very important discrepancies.

Lately several authors (Lothe & Pound 1962; Oriani & Sundquist 1963; Courtney 1965) have emphasized that important terms are missing in the expression for the free energy of formation ΔG^* . The most important of these are the free energy changes for 'gasification' of the cluster. These terms have been evaluated using the partition functions for rotation, translation and vibration. Unfortunately, there is not yet general agreement on how this should be done and the factors which predict the increase in nucleation rate due to gasification vary over a wide range. The essential problems are whether or not the cluster can be considered rigid and, if so, how to conserve the total number of degrees of freedom, once the translational and rotational degrees of freedom are recognized. Depending on how these effects are treated the nucleation rate equation may need to be multiplied by a factor as large as 10^{17} .

3. Growth of liquid clusters or drops

In typical nozzle condensations, the mass of the critical-sized nucleus is very much smaller than the mass of liquid which condenses upon it as the supersaturation of the vapour reduces rapidly to a value near unity. It is therefore very important to be able to calculate drop growth in order to determine the effect of condensation on the nozzle gas dynamics.

For growth two different coefficients are in general significant (both loosely referred to as accommodation coefficients).

3.1. Condensation coefficient

Defining ξ as the fraction of the arriving molecules which enter the surface we may write that the condensing mass flux \dot{m}_c is

$$\dot{m}_c = \xi P / \sqrt{(2\pi RT)}.$$

For a surface in equilibrium, the condensing and evaporating mass fluxes must of course be equal so we could equally well call ξ the evaporation coefficient.

Owing to widespread practical interest in evaporation and vacuum distillation, data on evaporation coefficients of a variety of substances are available and are discussed in the Appendix. The value obtained by Alty & Mackay (1935), $\xi = 0.04$, has been used in this study.

3.2. Thermal accommodation coefficient

If $\xi < 1$, the particles which simply reflect from the liquid surface without passing through it may significantly transport energy from the surface depending on the thermal accommodation coefficient α . This is defined, following Wachman (1962), as

$$\alpha = \lim_{\Delta T \rightarrow 0} (T_r - T) / \Delta T,$$

in which T is the temperature of the ambient gas, ΔT is the temperature difference between the surface and the ambient gas, and T_r is the temperature of the stream

of molecules receding from the surface. Very few data appear to be available on thermal accommodation at gas-liquid interfaces. However, Alty & MacKay (1935) have concluded from measurements on evaporating water drops that the reflected vapour molecules attain thermal equilibrium with the surface before leaving it. Alty (1936) asserts that 'in spite of the apparent difficulty experienced by the vapour molecules of some liquids in penetrating the liquid surface, there is no known exception to the rule that the accommodation coefficient of a vapour at the surface of its liquid has always the value unity'. This conclusion contrasts with information that for clean metal surfaces it is usual to find $\alpha \ll 1$ (see Wachman 1962). However, it has been found that α may rise by an order of magnitude due to adsorption of gas layers on these metal surfaces. The surface of a relatively thick adsorbed layer might behave somewhat like a liquid surface so perhaps it is not surprising that the liquid-surface accommodation coefficient should be high.

3.3. Drop growth equations

Typically the critical-sized nucleus given by equation (2) is two or three orders of magnitude less than the mean free path. Also the average drop size is usually still less than one mean free path after passing through the nozzle so that we use the results of the kinetic theory for predicting mass and energy fluxes to and from the drop surface.

Ignoring the motion of the drop itself the mass flux to the surface per unit area per unit time is $P/\sqrt{(2\pi RT)}$. Of this a fraction ξ condenses on the surface while $1 - \xi$ is reflected. The average specific energy of the arriving molecules is KRT , where K may be taken to be $\frac{1}{2}(\gamma + 1)/(\gamma - 1)$, and T is the temperature of the ambient vapour, which is assumed uniform. The reflected molecules will leave the surface at a temperature given by $T + \alpha(T_D - T)$, where T_D is the drop temperature. Since the drop is so small, temperature variations within it may be ignored. The rate at which mass evaporates from the surface will be given by

$$(1 - \xi) P_D / \sqrt{(2\pi RT_D)},$$

where P_D is the (hypothetical) ambient pressure which would be necessary to keep the drop in equilibrium, both drop and vapour having temperature T_D . Using the Helmholtz equation this pressure is

$$P_D = P_\infty(T_D) \exp\{2\sigma/(\rho_L RT_D r)\}, \quad (4)$$

in which r is the drop radius and $P_\infty(T_D)$ is the flat-film saturation pressure corresponding to the temperature T_D . With these in mind the mass and energy fluxes to and from the growing drop are given in table 2.

The rate at which the drop grows is the difference between the condensation and evaporation rates, and it may easily be shown that

$$\frac{dr}{dt} = \frac{\xi}{\rho_L} (\beta - \beta_D), \quad (5)$$

which $\beta = P/\sqrt{(2\pi RT)}$, $\beta_D = P_D/\sqrt{(2\pi RT_D)}$, and ρ_L is the density of the liquid.

The net rate of energy flux to the drop must be balanced by the rate of increase of its internal energy, which is given by

$$\frac{4}{3}\pi r^3 \rho_L c \frac{dT_D}{dt} + 4\pi r^2 \frac{dr}{dt} \rho_L U_{fD},$$

in which c is the specific heat of the liquid, and U_{fD} is its internal energy at temperature T_D . Since T_D will not usually be very much greater than T , we may approximate U_{fD} (taking the vapour to be a perfect gas) by

$$U_{fD} \simeq h_{fD} = \frac{\gamma}{\gamma - 1} RT - h_{fg},$$

in which γ is the specific-heat ratio of the vapour.

Flux per unit area	Arriving vapour		Leaving vapour	
	Condensing	Reflecting	Reflecting	Evaporating
Mass	$\xi P/\sqrt{(2\pi RT)}$	$(1 - \xi) P/\sqrt{(2\pi RT)}$	$(1 - \xi) P/\sqrt{(2\pi RT)}$	$\xi P_D/\sqrt{(2\pi RT_D)}$
Energy	$\{\xi P/\sqrt{(2\pi RT)}\} KRT$	$\{(1 - \xi) P/\sqrt{(2\pi RT)}\} KRT$	$\{(1 - \xi) P/\sqrt{(2\pi RT)}\} \times KR\{T + \alpha(T_D - T)\}$	$\{\xi P_D/\sqrt{(2\pi RT_D)}\} KRT_D$

TABLE 2

If the condensing vapour is mixed with a non-condensing carrier gas there will be an additional net energy flux away from the growing drop of magnitude per unit area of

$$\{P_c/\sqrt{(2\pi R_c T)}\} \alpha_c KR(T_D - T),$$

in which P_c is the partial pressure of the carrier gas, R_c its gas constant, and α_c is the thermal accommodation coefficient for the carrier gas on the liquid surface. The influence of this term may be very large. In condensing-steam flows, the drops are so hot that the rate at which molecules evaporate is nearly as large as the rate at which they condense. On the other hand, with water vapour in an air nozzle, the air molecules transport sufficient energy from the drop surface to cool it so that re-evaporation is negligible.

Now, summing up the energy flux and storage terms, we obtain an energy-conservation equation for the growing drop:

$$\frac{1}{3}\rho_L \frac{rc}{RT} \frac{dT_D}{dt} = K\xi\beta(1 - \beta_D T_D/\beta T) - K(1 - \xi)\beta\alpha\{(T_D/T) - 1\} - \beta_c K\alpha_c\{(T_D/T) - 1\} - \rho_L \frac{dr}{dt} \left(\frac{\gamma}{\gamma - 1} RT - h_{fg} \right) / RT,$$

in which $\beta_c = P_c/\sqrt{(2\pi R_c T)}$, and γ is the specific heat ratio for the vapour.

The drops are so extremely small that the term on the left-hand side is negligible. The ratio of this term to the last one on the right-hand side is

$$Z = \frac{rc dT_D/dt}{(3RT dr/dt)(\lambda - 1)\gamma/(\gamma - 1)},$$

where $\lambda = (\gamma - 1)h_{fg}/\gamma RT$. Using the typical numbers

$$\xi = 1, \quad dr/dt \sim 1 \text{ cm/sec}, \quad r \sim 100 \times 10^{-8} \text{ cm}, \quad T \sim 100^\circ\text{C},$$

$$\gamma/(\gamma - 1) \sim 4, \quad \lambda \sim 4, \quad c \sim 1 \text{ cal/g }^\circ\text{C}, \quad dT_D/dt \sim 5 \times 10^6 \text{ }^\circ\text{C/sec},$$

we obtain $Z < 0.001$.

Thus the rate at which energy must be added to a drop to change its temperature as it grows is entirely negligible relative to the rate at which the condensing liquid imparts its latent heat to the drop. Neglecting the dT_D/dt term, the energy equation may be written

$$0 = K\xi(1 - \beta_D T_D/\beta T) - K(1 - \xi)\alpha\{(T_D/T) - 1\} + \xi(1 - \beta_D/\beta)(\lambda - 1)\gamma/(\gamma - 1) - (\beta_c/\beta)K\alpha_c\{(T_D/T) - 1\}. \quad (6)$$

For a growing drop under these conditions (high Knudsen number) equations (5) and (6) may be used to determine the drop radius r and temperature T_D as a function of time.

To apply these equations to condensation drops in a flowing stream, it would be necessary to know the coefficients ξ, α . Further, in principle, it would be necessary to calculate simultaneously the growth rates of many drops (of differing size) unless a suitable average can be taken. However, the dependence of P_D or r effectively vanishes before the drop has typically grown very much. For example, for $T_D = 100^\circ\text{C}$, $\sigma = 56 \text{ dynes/cm}$, $\rho_L = 1 \text{ g/cm}^3$, the ratio $P_D/P_\infty(T_D)$ is 3.77 for $r = 5 \text{ \AA}$ but only 1.39 for $r = 20 \text{ \AA}$. The drops typically grow much larger than the latter value so that it is satisfactory to let $P_D = P_\infty(T_D)$.

In applying these equations to a flowing gas stream coagulation has been ignored. Studies on smoke coagulation (Whytlaw-Gray 1932) indicate that this assumption may not be justified. Nevertheless, coagulation would not have much effect on the net condensation rate unless the total surface area were reduced by at least an order of magnitude. Relative motion between the condensation drops and the bulk of the gas stream has been neglected since the drops are so small.

Typical results of using these equations to calculate growth rates of a single drop in an infinite environment of constant supersaturation are shown in figures 1-3. In these calculations the initial radius, i.e. the radius corresponding to 100% probability of growth, has been taken as 1.3 times the critical radius.

It may be seen from figure 1 that the drop growth rate is hardly affected by changing ξ as long as $\alpha = 1$. For low values of α the growth rate goes sharply down with ξ . Figure 2 shows that after reaching a size of approximately $3 \times 10^{-7} \text{ cm}$ the drop-growth rate is linear with time (the ambient pressure and temperature being unaffected).

In Figure 3 it is seen that the drop temperature increases fairly rapidly in most cases toward the saturation value corresponding to the ambient pressure. It may be noted that, since we have assumed here a vapour of constant supersaturation, the drop continues to grow even though the surface temperature exceeds the saturation value. The condensation rate $P/\sqrt{(2\pi RT)}$ is greater than the evaporation rate $P_D/\sqrt{(2\pi RT_D)}$ because $P_D < P$.

Although doubt can be cast on certain measurements of ξ and α which have been made it does appear that, for H_2O , ξ should be very low and α should be around unity.

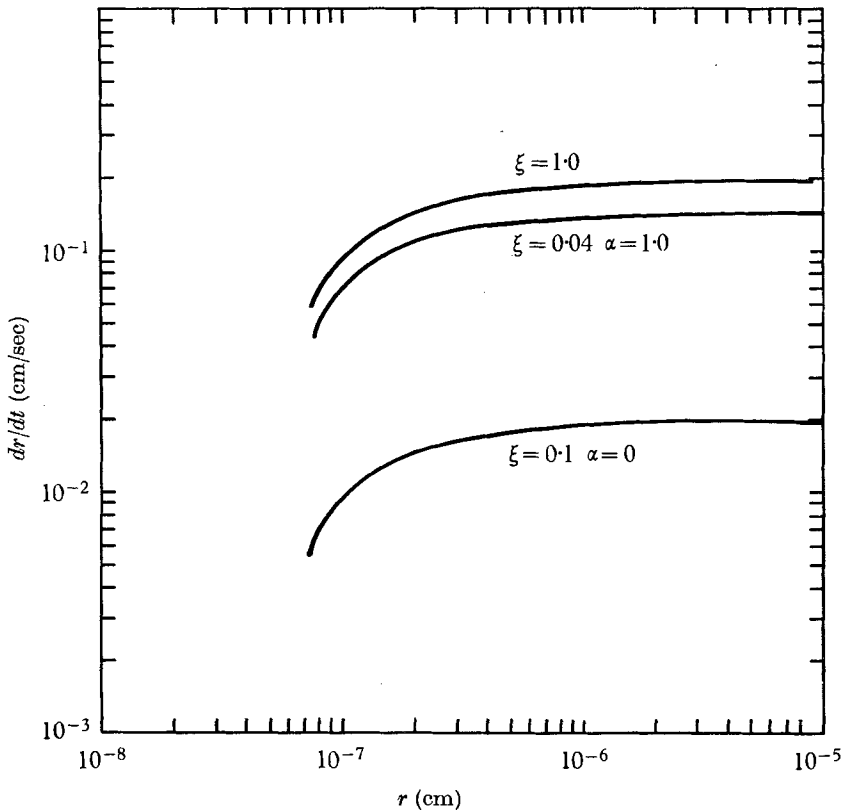


FIGURE 1. Growth of a liquid drop in H_2O vapour at 1 atm and 68°C , $P/P_\infty = 4.24$. ξ is the condensation coefficient, α the thermal accommodation coefficient.

If ξ were actually unity then α would be irrelevant and, as has been shown, the rate of drop growth would be little different.

If α is actually very low then the value of ξ is extremely important. There seems no reason why α should not be unity for a liquid in contact with its own vapour, but the direct experimental evidence for this is very thin. However, indirect evidence is considerable; since α would have a very strong effect on the growth rate (at low ξ) it would have a strong effect on the rate of pressure rise during a condensation 'shock'. It will be shown later that only high values of α (again ξ being low) are compatible with experimental pressure distributions.

4. Gas dynamics

The effect of the condensation process on the gas dynamics may be easily computed if the flow is assumed to be one-dimensional. For the experimental nozzles to be discussed, this is a fairly good approximation since the boundary layers must have been small relative to the throat width and the rate of divergence

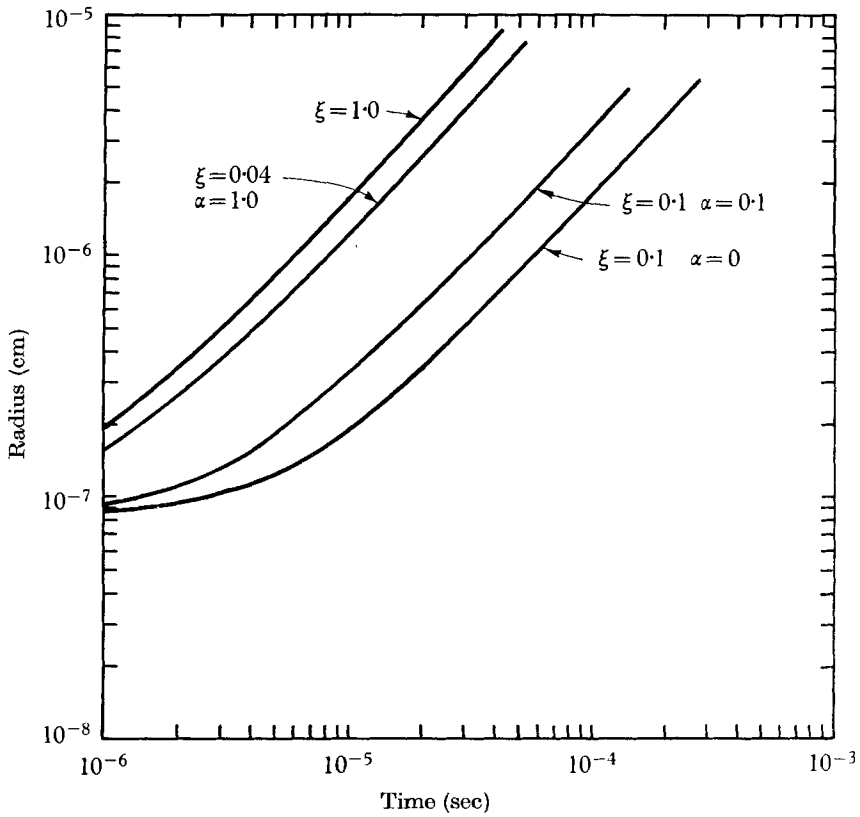


FIGURE 2. Growth of a liquid drop in H_2O vapour at 1 atm and 68°C , $P/P_\infty = 4.24$.

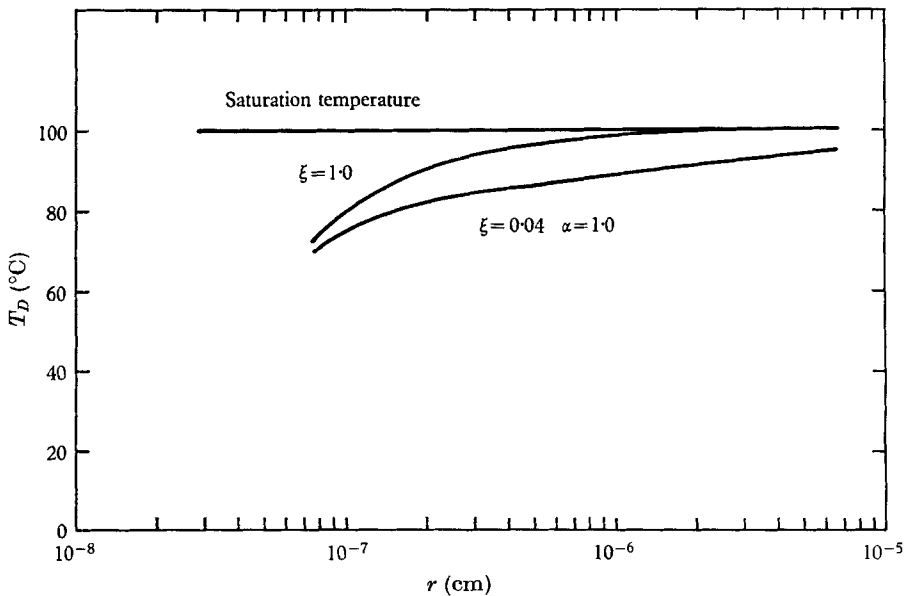


FIGURE 3. Growth of a liquid drop in H_2O vapour at 1 atm and 68°C , $P/P_\infty = 4.24$.

was generally moderate. At the throat the boundary-layer thickness would have been of order $\sqrt{(vx/U)}$ (assuming it to be laminar). Taking $v = 2 \times 10^{-5}$ ft.²/sec, $x = 0.1$ ft., $U = 10^3$ ft./sec, $\sqrt{(vx/U)} \sim 10^{-3}$ in. or at most 1 or 2% of the throat width. Thus the boundary layer is typically thin. Also it has little effect on the condensation process since, unless it is cooled strongly, most of it will be superheated and therefore free of nuclei.

For one-dimensional flow through the nozzle, the continuity, momentum and energy equations for the flow may be expressed as follows:

Continuity $\dot{m} = \rho A U / (1 - \mu),$ (7)

Momentum $-A dp = \dot{m} du,$ (8)

Energy $c_p dT + u du = h_{fg} d\mu,$ (9)

in which \dot{m} is the total flow rate (mass/sec), ρ the vapour density (approximately given by $\rho = P/RT$), A the cross-sectional area of the stream, u the velocity (the liquid drops are assumed to have negligible slip), μ the ratio by mass of liquid and vapour, and c_p the specific heat.

The area A in these equations is of course the effective area of the flow, i.e. the actual area minus the boundary-layer-displacement area. In writing equation (9), it has been assumed that $\mu \ll 1$ so that the specific heat of the mixture is the value for the vapour. In a typical steam expansion the vapour has returned essentially to equilibrium ($P/P_\infty \rightarrow 1$) before μ exceeds 0.03 or 0.04.

The relative rate of formation of liquid along the nozzle may be derived as follows. A nucleus formed at some position, x_1 , in the nozzle with an initial radius r_0 will grow to a size

$$r_0 + \int_{x_1}^x \frac{1}{u} \frac{dr}{dt} dx_2$$

by the time it reaches position x . Its surface area at x will then be

$$4\pi \left[r_0 + \int_{x_1}^x \frac{1}{u} \frac{dr}{dt} dx_2 \right]^2.$$

The total number of nuclei formed per second in a volume $A(x_1) dx_1$ is just $I(x_1) A(x_1) dx_1$, and therefore the rate at which liquid is condensed in the volume $A(x) dx$ on nuclei originating in the volume $A(x_1) dx_1$ is just

$$\rho_L 4\pi \left[r_0 + \int_{x_1}^x \frac{1}{u} \frac{dr}{dt} dx_2 \right]^2 I(x_1) A(x_1) dx_1 \frac{dr}{dt} \frac{dx}{u}.$$

Taking account also of the (very small) rate of condensation at x due to nucleation at x we have

$$\frac{d\mu}{dx} = \frac{4\pi\rho_L}{\dot{m}} \left[\int_0^x \left(r_0 + \int_{x_1}^x \frac{1}{u} \frac{dr}{dt} dx_2 \right)^2 I(x_1) A(x_1) \frac{1}{u} \frac{dr}{dt} dx_1 + \frac{1}{3} r_0^3 I(x) A(x) \right].$$
 (10)

As was shown in § 3 the growth rate is essentially independent of cluster size for nuclei greater than perhaps 30×10^{-8} cm. Since this is relatively small compared with the size a drop might reach in passing through the nucleation zone, it is probably acceptable to use the large-drop growth rate (independent of size) as a first approximation for dr/dt in equation (10). As a second and hopefully

better approximation, a drop-growth rate has been calculated by using the 'surface-averaged' radius of all clusters at a given cross-section. The overall results of condensation on the nozzle pressure distribution were the same for both approximations.

Equations (7) to (10) have been rewritten as follows for numerical integration with a Runge-Kutta-Merson integration procedure:

$$\frac{dP}{dx} = P \left\{ (\lambda - 1) \frac{d\mu}{dx} - \frac{1}{A} \frac{dA}{dx} \right\} \left\{ 1 - (1 - \mu) [(\gamma - 1)/\gamma + 1/\gamma M^2] \right\}, \quad (11)$$

$$\frac{dT}{dx} = T \left\{ \lambda \frac{d\mu}{dx} + \left(\frac{\gamma - 1}{\gamma} \right) (1 - \mu) \frac{1}{P} \frac{dP}{dx} \right\}, \quad (12)$$

$$\frac{dM}{dx} = M \left\{ -(1 - \mu) \frac{1}{P} \frac{dP}{dx} \left(\gamma M^2 \right) - \frac{1}{2T} \frac{dT}{dx} \right\}, \quad (13)$$

$$\frac{d\mu}{dx} = \frac{\rho_L}{\dot{m}} \left\{ Q_1 \frac{1}{u} \frac{dr}{dt} + \frac{4\pi}{3} I A r_0^3 \right\}, \quad (14)$$

$$\frac{dQ_1}{dx} = \left\{ Q_2 \frac{1}{u} \frac{dr}{dt} + 4\pi I A r_0^2 \right\}, \quad (15)$$

$$\frac{dQ_2}{dx} = \left\{ Q_3 \frac{1}{u} \frac{dr}{dt} + 8\pi I A r_0 \right\}, \quad (16)$$

$$\frac{dQ_3}{dx} = 8\pi I A, \quad (17)$$

in which Q_1 , Q_2 and Q_3 are merely variables introduced to reduce the integro-differential equation (10) to four simultaneous first-order differential equations, $\lambda = h_{fg}/c_p T$ as before, and M is the Mach number. A cluster of size r^* has a probability of growth of 0.5. By the time it grows to $1.3r^*$ the probability is very near unity so that this has been used as the starting radius r_0 . However, if r_0 were taken as zero it would not noticeably alter the numerical results of these equations since r_0 is generally much less than the radius of the cluster after a period of growth.

The nucleation-rate variable I appearing in equations (15) to (17) has been calculated from equation (3) with, or without, the use of a constant multiplicative factor (see § 3) to account for the possible effects of cluster gasification.

The average drop-growth rate has been calculated from equation (5) using equation (4) to determine the pressure P_D . The average drop radius which has been used in equation (4) is the 'surface-averaged' radius \bar{r} given by

$$\bar{r} = \sqrt{(2Q_1/Q_3)}.$$

The drop temperature which has been used in equation (4) is the one which satisfies equation (6) for given values of P , T , \bar{r} , λ , α , ξ . If, as a somewhat simpler approximation, the drop-growth rate is assumed independent of size, $P_D \rightarrow P_\infty(T_D)$, and equations (5) and (6) then are independent of size. A still more approximate assumption would be to assume (like Oswatitsch) that T_D is always the saturation value corresponding to pressure P . Then equation (6) is unnecessary, and the drop-growth rate can be calculated simply from equation (5). The last approximation has not been used in the present calculations.

5. Experimental results

Experimental data on the condensation of steam have been obtained by different workers in nozzles whose area distributions are indicated in figure 4. It will be seen that the relative expansion rates $(1/A)(dA/dx)$ differ by a factor of 4 or 5. In all cases the throat diameter would have been an order of magnitude larger than the boundary-layer thickness so that most of the flow would have expanded isentropically.

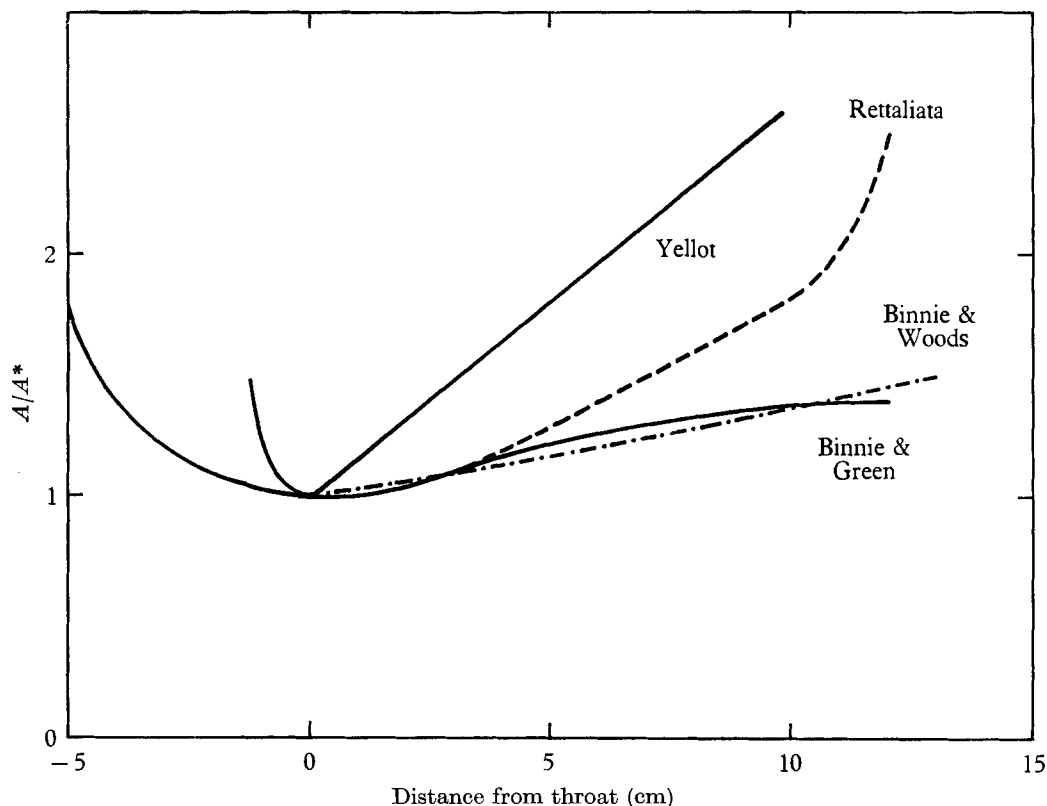


FIGURE 4. Area distributions for experimental nozzles. Throat sizes (cm²): Binnie & Green, 1.908 × 1.31; Binnie & Woods, 3.53 × 0.965; Rettaliata, 1.6 × 1.6; Yellot, 1.27 × 2.54.

The experimental results of Binnie & Green (1943) (figure 5) are particularly valuable in that they clearly reveal the pressure distribution in the nucleation region. In plotting figure 5 the area ratio is the isentropic one; this is determined from the pressure distribution measured with dry vapour expansion (using the assumption that condensation does not affect the boundary-layer thickness). The pressure rise in the condensation zone is not more than 10%, and the boundary layers are likely to be mostly free of condensation, so this assumption is probably valid. To obtain large pressure rises it is necessary (as may be shown from equation 11) to have condensation occur at a Mach number fairly close to unity. However, if the Mach number just before condensation is too close to 1, then it will approach 1 in the zone itself. In this case choking at the geometric

throat will be inhibited, and the flow may oscillate as observed by Schmidt (1962) with an interferometer and high-speed camera.

The shape of the nozzle does affect the change in pressure distribution due to condensation, as one would expect from equation (11). However, for steam this factor is not of great importance. Figure 6 shows theoretical computations of the effect of nozzle shape on pressure distribution for two different nozzles whose expansion rates differ by a factor of 5. As might be expected in proceeding along a given isentrope, the effects of condensation are noticeable at somewhat higher

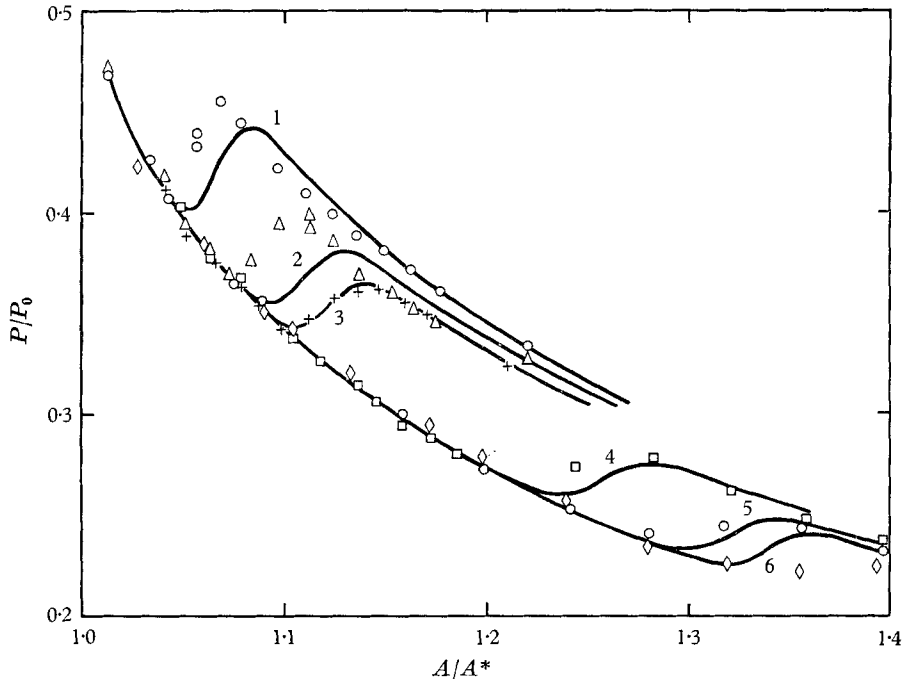


FIGURE 5. Pressure ratio as a function of effective area ratio. Experimental data taken from Binnie & Green (1942). Theoretical curves calculated for a nucleation rate given by equation (3), flat-film value of the surface tension, $\xi = 0.04$, $\alpha = 1.0$. \circ , Experimental points for $P_0 = 0.647$ atm, $T_0 = 101^\circ\text{C}$ and corresponding theoretical curve 1; \triangle , 0.652 atm, 108°C , theoretical curve 2; $+$, 1.022 atm, 126°C , theoretical curve 3; \square , 0.646 atm, 127°C , theoretical curve 4; \circ , 0.656 atm, 136°C , theoretical curve 5; \diamond , 0.935 atm, 153°C , theoretical curve 6.

pressures for the nozzle whose expansion rate is lower. However, the difference is not very large. With this in mind, it is not surprising to find that, for a given nozzle, the pressure ratio at the minimum point preceding the pressure rise depends very little on inlet conditions for a given isentrope. From equation (11) it is seen that the pressure minimum requires

$$(\lambda - 1) \frac{d\mu}{dx} = \frac{1}{A} \frac{dA}{dx}.$$

The rate at which moisture forms $d\mu/dx$ is such a strong function of pressure ratio (i.e. supersaturation) that the pressure ratio at the minimum depends very little on the local expansion rate $(1/A)(dA/dx)$. This has been recognized

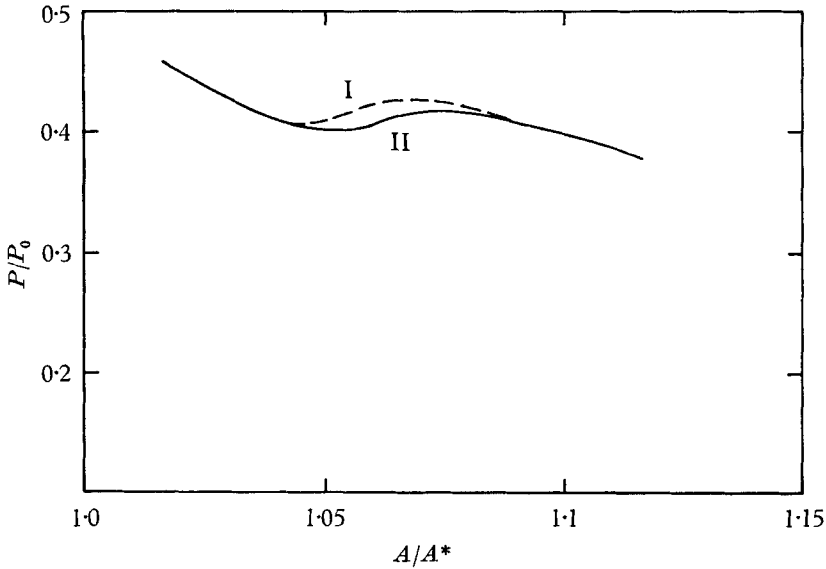


FIGURE 6. Effect of the nozzle shape on the pressure distribution for steam condensation. Curve I, Binnie & Green nozzle; curve II, Yellot nozzle (see figure 4) with $P_0 = 8$ atm, $T_0 = 201$ °C.

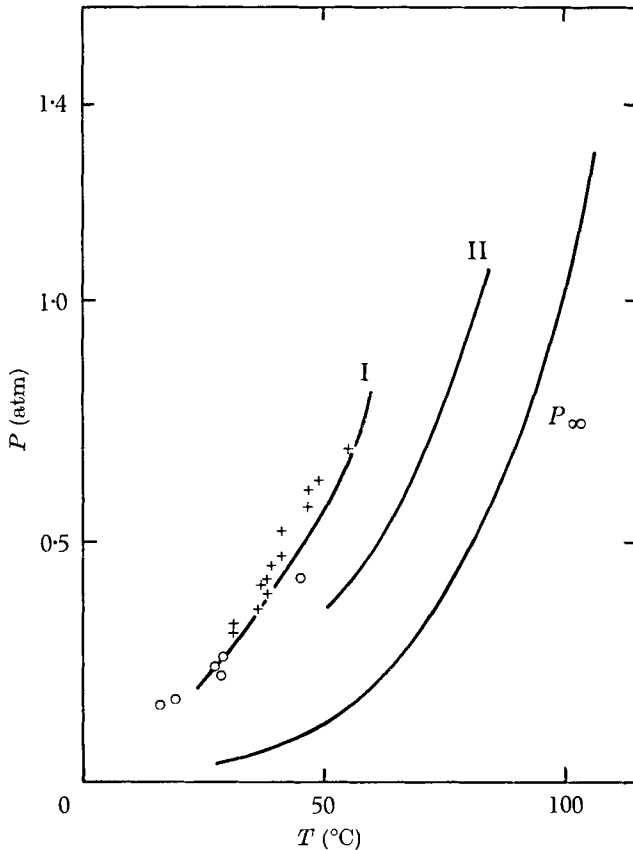


FIGURE 7. Incidence of condensation. Curve I, calculation based on equation (3) with $\sigma/\sigma_\infty = 1$; curve II, equation (3) times 10^{17} with $\sigma/\sigma_\infty = 1$. O, Experimental points from Binnie & Green; +, from Binnie & Wood.

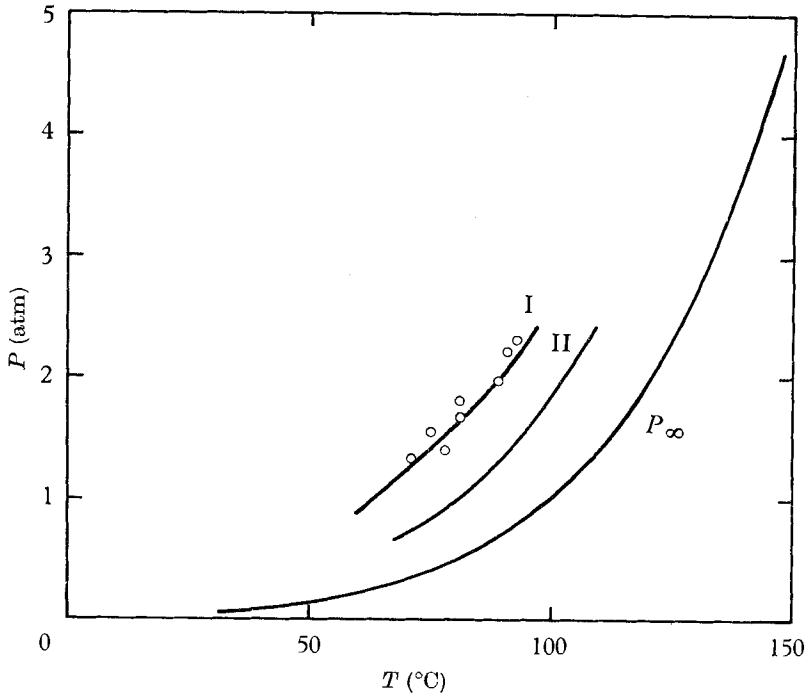


FIGURE 8. Incidence of condensation. Curve I, calculation based on equation (3) with $\sigma/\sigma_\infty = 1$; curve II, equation (3) times 10^{17} with $\sigma/\sigma_\infty = 1$. \circ , Experimental points from Rettaliata.

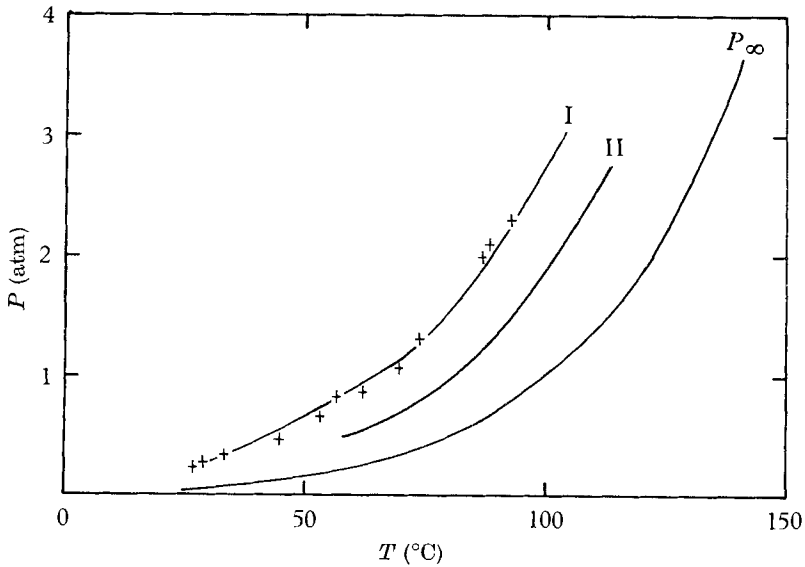


FIGURE 9. Incidence of condensation. Curve I, calculation based on equation (3) with $\sigma/\sigma_\infty = 1$; curve II, equation (3) times 10^{17} with $\sigma/\sigma_\infty = 1$. $+$, Experimental points from Yellot.

for a long time, as the empirical results of Yellot & Holland (1937) clearly demonstrate.

In the data obtained by Binnie & Woods (1938), and Yellot (1934) the shape of the pressure distribution in the nucleation zone is not well known, though the point of condensation incidence is, and these data are shown on figures 7-9. Upon superimposing the data of figures 7-9 it is found that they occupy a common band. Thus the foregoing observations on the effect of nozzle-expansion rate are generally supported by the data.

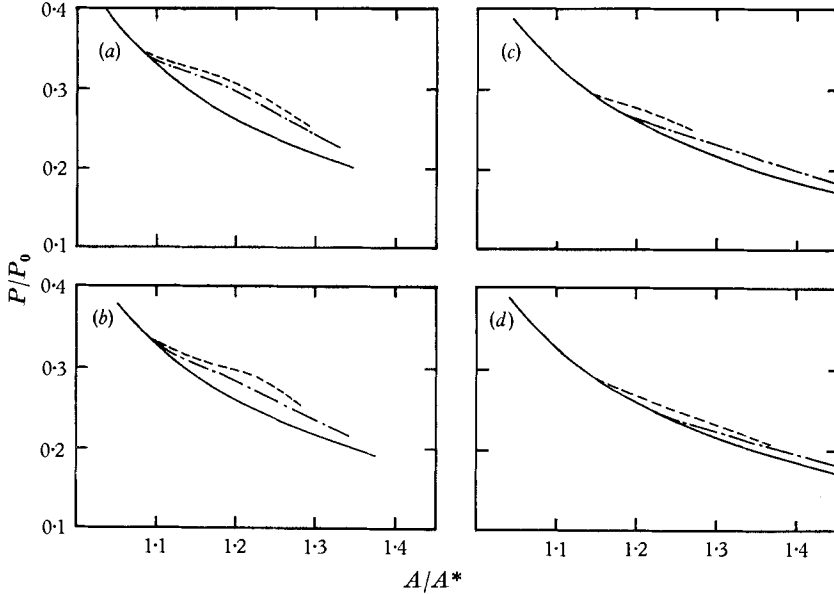


FIGURE 10. Condensation of water vapour in an air nozzle. —, Isentropes; ---, data from Wegener & Pouring; — · —, theoretical curve based on equation (3) with $P = P_{\text{vapour}}$, $\sigma = \sigma_{\infty}$, $\alpha = 1.0$. (a) $T_0 = 23^\circ \text{C}$, $P_0 = 762 \text{ mmHg}$, $\omega_0 = 0.0049$; (b) $T_0 = 22^\circ \text{C}$, $P_0 = 755 \text{ mmHg}$, $\omega_0 = 0.0044$; (c) $T_0 = 25^\circ \text{C}$, $P_0 = 759 \text{ mmHg}$, $\omega_0 = 0.0035$; (d) $T_0 = 25^\circ \text{C}$, $P_0 = 747 \text{ mmHg}$, $\omega_0 = 0.0029$. ω_0 is the initial specific humidity.

Figure 10 shows test data obtained by Wegener & Pouring (1964). For the data shown, the condensation zone was downstream of the nozzle throat. The partial pressure of the water vapour was about three orders of magnitude lower than for the typical steam measurements so the absolute nucleation rate was around six orders lower and the pressure rise due to condensation was much less. For this reason it is somewhat difficult to tell from the measured pressure distribution where condensation began.

Figure 11 shows experimental data obtained by Head (1949) on the condensation of water vapour in nitrogen. The rate of divergence $(1/A)(dA/dx)$ of the nozzle used by Head was somewhat larger than that of the Wegener-Pouring nozzle. For water vapour condensing in a carrier gas, the effect of nozzle shape can be much more marked than with steam. The vapour pressures are typically two or three orders of magnitude less, and the growth rates are therefore considerably lower so that the transition from dry to equilibrium wet vapour is considerably slower and more dependent on the time of residence of the fluid within the nozzle.

6. Theoretical results

Using the procedures outlined in §§ 2–4, theoretical calculations were made for the conditions of the experiments discussed in § 5. For a first attempt the most elementary approach was used; i.e. the Frenkel–Zeldovitch equation was used to predict nucleation rate with no correction being made for the surface energy of the clusters (and no account being taken of the gasification factor). It was found that this procedure, which incorporated no arbitrary adjustments or ‘corrections’, led to a surprisingly accurate prediction of all the experimental data, including that obtained in both steam and most-air nozzles.

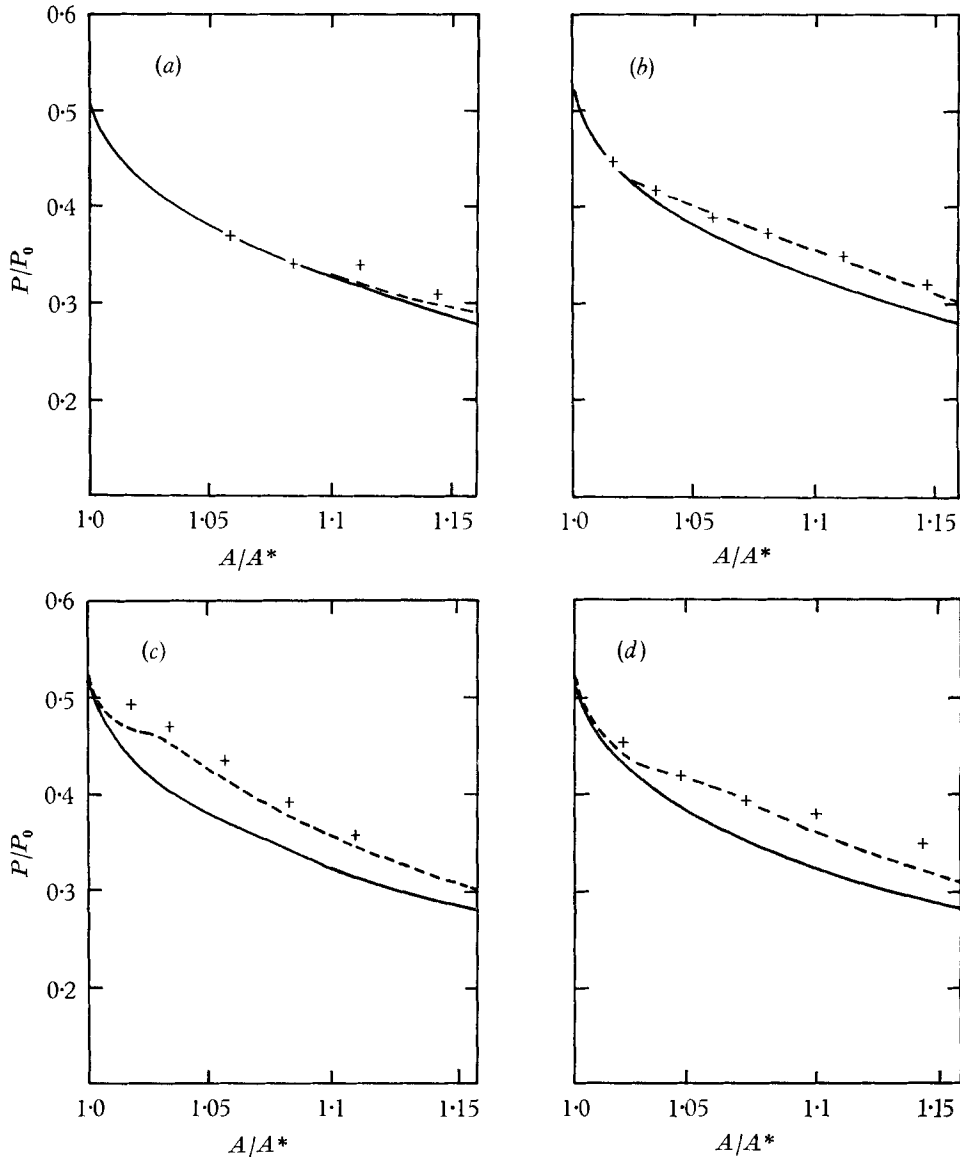


FIGURE 11. For legend see facing page.

When the rate correction obtained by Lothe & Pound (1962) was used, the results were quite far removed from the experimental data. The only way in which the two could be reconciled would be a large compensating effect of cluster size on surface energy (an increase of perhaps 30%). A decrease in surface energy as predicted by the Kirkwood-Buff equation would be entirely incompatible with experimental data using either of the rate calculations discussed above.

From figures 5 and 7-9, it will be seen that the calculations which use the Frenkel-Zeldovitch equation agree with the steam data as well as could reasonably be expected from the accuracy and reproducibility of the data.

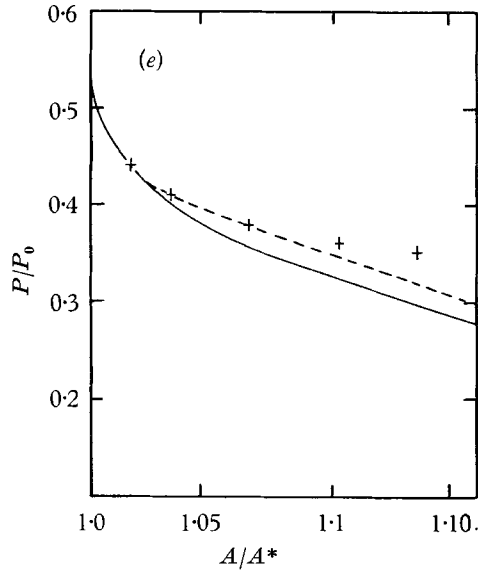


FIGURE 11. Condensation of water vapour in nitrogen, —, Isentrope; ---, theoretical curve based on equation (3) with $\sigma/\sigma_\infty = 1$; +, data from Head. (a) $T_0 = 24^\circ\text{C}$, $P_0 = 1.65$ atm, $\omega_0 = 0.0036$; (b) $T_0 = 24^\circ\text{C}$, $P_0 = 2.68$ atm, $\omega_0 = 0.0039$; (c) $T_0 = 24^\circ\text{C}$, $P_0 = 3.680$ atm, $\omega_0 = 0.00374$; (d) $T_0 = 24^\circ\text{C}$, $P_0 = 3.02$ atm, $\omega_0 = 0.00388$; (e) $T_0 = 24^\circ\text{C}$, $P_0 = 3.38$ atm, $\omega_0 = 0.0031$.

Figures 10 and 11 show the results of theoretical calculations to compare with the experimental data of Wegener & Pouring (1964) and Head (1949). In both cases the agreement is quite reasonable considering experimental uncertainties. Figure 12 shows that the rate correction of Lothe & Pound leads to a result far removed from the data. It will be noted from figure 12 that the effect of the nozzle shape on the locus of incident condensation is quite noticeable. Moreover, the theoretical prediction is, on the whole, quite consistent with the experimental evidence.

Figure 10 shows a few theoretical results to compare with the experimental data of Wegener & Pouring (1964).

Figures 13-15 illustrate the effect of arbitrary variations in physical variables upon the theoretical result (for steam). Figure 13 shows that the shape of the pressure distribution as well as the point of apparent incidence is almost independent of the condensation coefficient ξ , as long as the accommodation coefficient

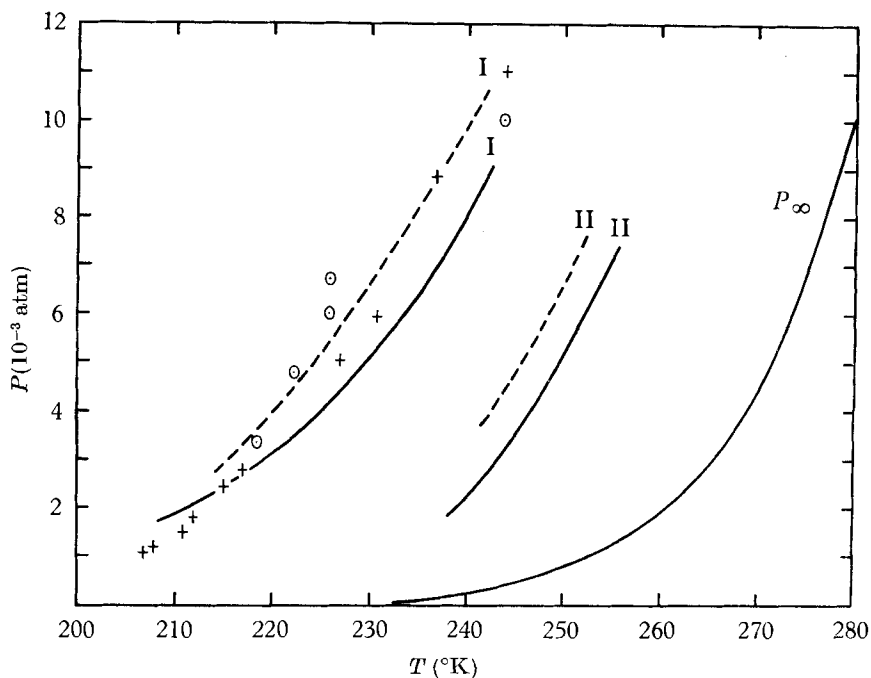


FIGURE 12. Incidence of condensation of water vapour. Curve I, equation (3) with $\sigma/\sigma_\infty = 1$; curve II, equation (3) times 10^{17} with σ/σ_∞ . ----, Head nozzle; —, Wegener & Pouring nozzle; \odot , data for air from Wegener & Pouring; +, data for nitrogen from Head.

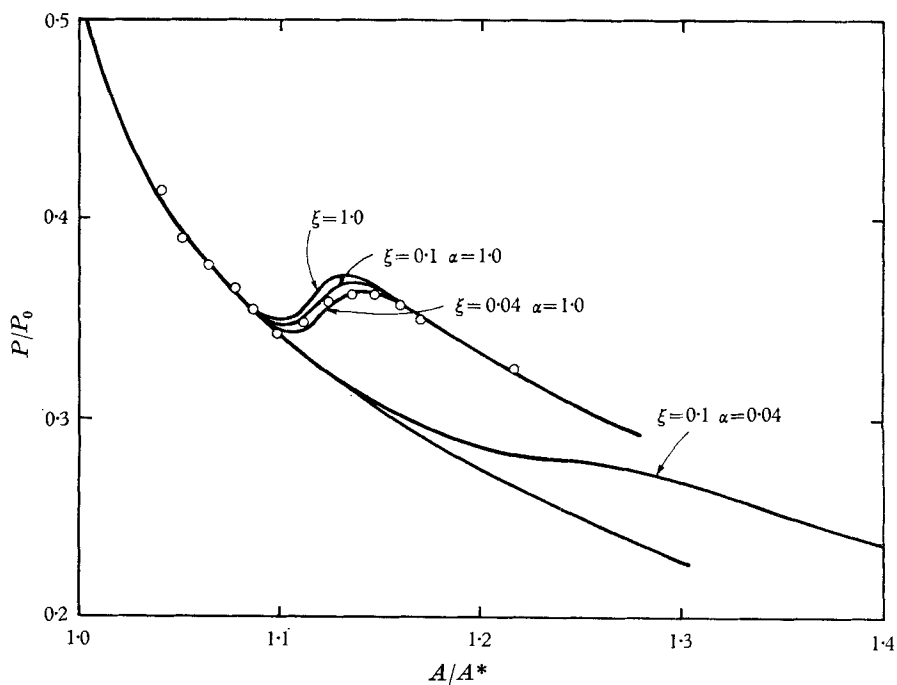


FIGURE 13. Effect of variations in the condensation coefficient ξ and in the thermal accommodation coefficient α on the shape of the pressure distribution (using equation (3) with $\sigma/\sigma_\infty = 1$). \odot , Data of Binnie & Green for $P_0 = 1.022$ atm, $T_0 = 126$ °C.

α is around unity. On the other hand, it is drastically altered if both ξ and α are much less than unity. Considering figure 13, it seems fairly clear that either ξ or α , or both, must be near unity and that for purposes of predicting the effects of condensation on nozzle gas dynamics it does not matter much which of these three alternatives is really the case.

Figure 14 simply illustrates the effect of a 10% change in the cluster surface energy on the predicted pressure distribution. This large effect emphasizes the

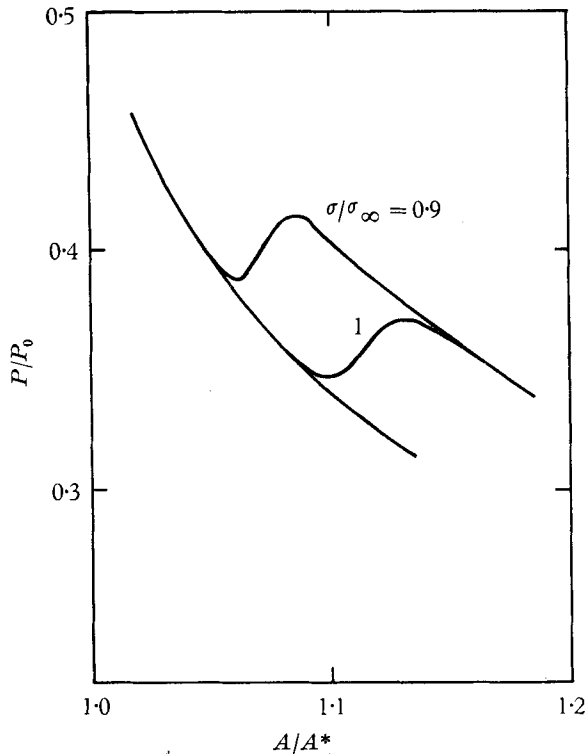


FIGURE 14. Influence of σ on the pressure distribution calculated for the nozzle of Binnie & Green.

need for accurate information on the temperature dependence of the surface tension. In the calculations described above, a linear variation of σ with T was used, i.e.

$$\sigma = 75.6 - 0.192(TC) \text{ dynes/cm.}$$

Figure 15 illustrates the large changes in pressure distribution due to multiplying the nucleation rate by even 10^5 or 10^{10} . Thus it is not difficult to determine from analysis of nozzle-condensation measurements the actual nucleation rates within perhaps two or three orders of magnitude.

7. Conclusions

- (i) Data on the condensation of steam in nozzles are abundant, quite consistent, and useful for testing nucleation theory on H_2O .
- (ii) Adequate drop-growth calculations must be made before theory and

experiments can be satisfactorily compared. Experimental results are consistent with independent evidence that, for the gas-liquid H_2O surface, the thermal accommodation coefficient α is near unity. In this case the value of the condensation coefficient is not of much importance, within reasonable limits.

(iii) The incidence of condensation in steam can be satisfactorily predicted by the classical liquid-drop-nucleation theory with (a) no account taken of the gasification concept, (b) no correction made for the dependence of surface tension on curvature. However, if these two effects do occur physically, they must fortuitously be equal and opposite in result (for H_2O).

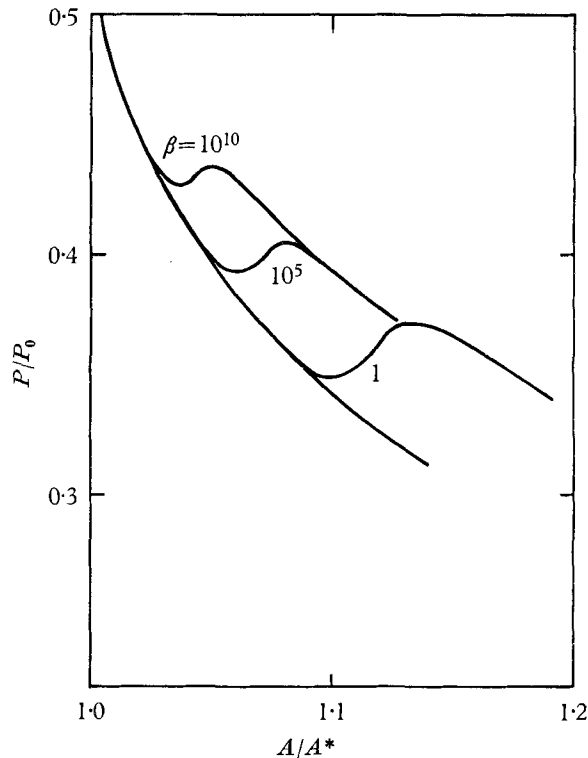


FIGURE 15. Effect of multiplying the nucleation equation by a constant factor β . The pressure distribution is calculated for the nozzle of Binnie & Green.

(iv) The incidence of condensation of moist air can be quite well predicted by the same methods used for steam. However, as pointed out by Wegener & Pouring (1964), the condensate for these flows may be in the form of ice particles whose surface energy would be even less certain than that of the liquid nuclei.

(v) If the Lothe-Pound treatment of the gasification concept is physically valid, then the surface tension of H_2O clusters must be appreciably greater than the flat-film value. The Kirkwood-Buff and Tolman correction is not supported by experimental evidence.

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Appendix. Data on evaporation coefficients

Table 3 shows various values of evaporation coefficients which have been reported for water liquid and ice.

Alty & MacKay (1935) made careful measurements on water drops evaporating into a vacuum and concluded that $\xi = 0.036$. Such a low value of ξ was thought

	Temperature range °C			
Liquid	0.036		15	Alty & MacKay (1935)
Liquid	0.02		100	Prueger (1940)
Liquid	0.43			Hickman (1954)
Ice	0.07		-20	Baranaev (1946)
Ice	0.94 ± 0.06	-85	60 -60	Tschudin (1946)
Ice†	0.44 to 0.63	-55 to	-51	Strickland-Constable & Bruce (1954)
Ice†	0.5 to 1.0	-41 to	-59	Kramers & Stemmerding (1953)

† These authors consider their results to confirm the conjecture that ξ is essentially unity for water ice.

TABLE 3. Measured evaporation coefficients, adapted from Paul (1962)

to be related to the high polar moment of the water molecule though none of the existing theories appear to be capable of predicting values of ξ (see Knacke & Stranski 1956) to any degree of certainty.

In recent years the findings of Alty & MacKay and the other reports of low values of ξ have been suspected† for three possible reasons.

Surface temperature

During evaporation into a vacuum the required heat flux to the surface may be relatively high, and, since this flux can be supplied only by radiation or conduction through the liquid, the surface temperature depression may be very large (and considerably larger than can be detected by thermocouples) so that the actual vapour pressure corresponding to the measurement of surface temperature could be much too high and the calculated value of ξ too low.

Littlewood & Rideal (1956) have considered this effect in detail and concluded that it would not be possible to measure the surface temperature accurately by thermocouples and that, for liquid surfaces, reported values of ξ different from unity could be very much too low for this reason. Alty & MacKay inferred the drop temperature by estimating its surface tension from its shape and size. Littlewood & Rideal felt that this, too, could have been in error since the surface

† Note added in proof: Recently Mills (A. F. Mills, 1965. The condensation of steam at low pressures, Ph.D. Thesis, College of Engineering, University of California, Berkeley) has re-examined experimental data on condensation coefficients for steam and concluded that there is no justification for assuming $\xi < 1$.

tension of a falling, evaporating drop might be supposed to differ from one in equilibrium. However the idea of a 'dynamic' surface tension has been shown by Wegener & Parlange (1964) to have no experimental support so that this does not appear to be a reason for doubting Alty & MacKay's results.

A very interesting example of this effect did arise in measurements by Sherwood & Cooke (1957) of ξ for naphthalene spheres evaporating into gases at low pressure. Neglecting the surface temperature depression, they obtained values of ξ in the range 0.05–0.16. Madden (1959) then pointed out that, even though the absolute evaporation rate and heat fluxes to the surface were low in that experiment, all the heat had to come in by radiation and that the temperature depression should have been of the order of 20 °C, so that the evaporation coefficient had been reported an order of magnitude low. In a sequel to this Sherwood & Johannes (1962) reported a new method of measuring the evaporation of naphthalene including a radiation detector for inferring the actual surface temperature. Essentially agreeing with Madden's estimate, they found that the actual value of ξ should have been around 0.88.

	Hexadecanol	Naphthalene	Biphenyl	Camphor	Thymol
ξ	1.00	0.88	0.60	0.18	0.14

TABLE 4

In further support of their suspicion, Littlewood & Rideal (1956) point out that reported values of ξ for liquid metals are all around unity (see Paul 1962). Since the metals have high thermal conductivity the surface temperature depression would be low and would not affect the determination of ξ .

Sherwood & Johannes (1962) obtained other values of ξ as given in table 4. They concluded, therefore, that, while Littlewood & Rideal had made an important point, not all liquids have ξ equal to unity and that (with the exception of hexadecanol), as the dipole moment increases, ξ does decrease.

Since H₂O does have a very high polar moment these results would tend to support Alty & MacKay's finding of a low value for ξ . In contrast, Tschudin (1946), in what Sherwood & Cooke describe as very careful work, obtains ξ for ice as around unity. There does not appear to be any reason why the values for ice and liquid water should be of the same magnitude.

Surface contaminations

Referring to the measurements of Knudsen (1915) on mercury, Hickman & Trevoy (1952) pointed out that, although ξ was close to unity for a clean surface, it could be very much less than that if the surface were dirty. With that in mind, they measured the evaporation rate from a laminar jet of liquid falling from a nozzle so that the surface was continuously created and should have been extremely clean. Using this apparatus Hickman (1954) obtained a value of ξ for water of 0.43 and said that it could have been no lower than 0.25 and might well have been much closer to unity. Hickman used a relatively high-speed jet and estimated that the surface temperature depression was only 1.5 °C.

Diffusion barrier

Burrows (1957) has pointed out that, for a number of experiments involving evaporation into a 'vacuum', the pressure was not quite low enough to prevent a significant number of collisions near the surface, so that particles return to the surface, and the evaporation rate appears lower than it really is. Taking this effect into account Burrows finds that the value of ξ for ice reported by Strickland-Constable & Bruce (1954) should really be revised to around unity.

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