

Selected Values of Critical Supersaturation for Nucleation of Liquids from the Vapor

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Selected values of critical supersaturations for homogeneous nucleation of droplets from the vapor and for heterogeneous nucleation of droplets on the natural stationary concentration of gaseous ions are tabulated and plotted, and a rationale is given for selection of these data.

Key words: Critical supersaturation; data evaluation; homogeneous nucleation; phase change.

1. Introduction

The critical supersaturation for nucleation from the vapor is defined as that ratio of actual partial pressure of vapor to equilibrium vapor pressure of bulk liquid for which the nucleation rate of droplets becomes appreciable. Thus in quoting a critical supersaturation it is also necessary to specify the approximate rate to which it corresponds if the statement is to have any meaning. It is found experimentally [e.g., C. T. R. Wilson, 1897, M. Volmer, 1939] and predicted theoretically [e.g., M. Volmer, 1939] that the nucleation rate increases very rapidly with increase in supersaturation, and this is the justification for speaking of a critical supersaturation. The writer knows of no reliable and precise measurements of actual nucleation rates in condensation, other than the approximate values needed to define the critical supersaturation. Of course, the critical supersaturation is a function of temperature, and tends to increase with decrease in temperature.

The experiments must be conducted in such a way that the nucleation of droplets does not occur on some unknown concentration of unidentified dust particles in the vapor. Another type of heterogeneous nucleation to be avoided is that catalyzed by unknown concentrations of unidentified ions, such as occurs in some experiments where artificial radiation is used to produce a concentration of gaseous ions. Meaningful information can perhaps be obtained from measurements of critical supersaturation on the stationary concentration of ions in naturally ionized air-vapor mixtures, and such data are included in the present review. Here, although the ionic species are by no means identified, the concentration is known to be of the order of 10^9 ion pairs per cubic centimeter [e.g., Loeb, 1934]. Even more meaningful results are measurements of critical supersaturation for homogeneous nucleation, i.e., uncatalyzed by ions and particulate matter. Such results may be compared with various quantitative theories for nucleation rate.

Measurements of critical supersaturation for nucleation of droplets in condensation are important in at least three connections:

- (a). They may be used to test various conflicting statistical mechanical treatments for the

nucleation process [e.g., see Lothe and Pound, 1968, and Reiss, Katz and Cohen, 1968, and Parlange, 1968]. This is of fundamental importance to our understanding of the thermodynamics of small bodies [e.g., Hill, 1964, Abraham and Pound, 1968].

- (b). Agreement of the results with theory is the foundation of our understanding of nucleation in all phase transformations, such as transformations in solids [e.g., Christian, 1965], crystallization from liquids [e.g., Strickland-Constable, 1968] and condensation from the vapor on substrates [e.g., Hirth and Pound, 1963].

- (c). Although formation of all rains and fogs is thought to occur by heterogeneous nucleation on particulate matter (dust particles), an understanding of homogeneous nucleation and heterogeneous nucleation on ions is of fundamental importance to our understanding of meteorological phenomena [e.g., Dufour and Defay, 1963, and Amelin, 1966].

There are at present three principal methods by which reliable measurements of critical supersaturations can be made:

- (a). The expansion cloud chamber method, which was invented by C. T. R. Wilson [1897].
- (b). The supersonic nozzle technique as developed by Wegener and coworkers [e.g., Wegener and Mack, 1958, and Wegener and Pouring, 1964] and by Hill [1966].
- (c). The diffusion cloud chamber method, which was developed by Franck and Hertz [1956] and by Katz and Ostermier [1967].

These techniques and their limitations will be described in the following section.

The purpose of the present work is to extract from the literature the correct values of critical supersaturation for homogeneous nucleation and for nucleation on gaseous ions of droplets from the vapor. Most of the data are for condensation of pure vapors. However the data of Flood [1934] for homogeneous nucleation from the water-ethanol binary are also included. The scope of this work originally included data for nucleation of crystallites from vapor; however no suitably reliable work of this type

could be found. One notes that the condensate usually occurs in liquid form, even though the temperature is below the thermodynamic freezing point; this is a consequence of Ostwald's "Law of Stages" [e.g., see Hirth and Pound, 1963].

Finally, in view of the controversies presently surrounding the theoretical developments in this field, no comparison will be made between the data and the theories, except to say that no single theory describes all substances.

2. Experimental Methods

2.1. The Expansion Cloud Chamber

The expansion cloud chamber was invented by Wilson [1897], and for many years it was the only device available for measuring critical supersaturations. In this method, a mixture of "inert carrier" gas such as air and the condensible vapor, usually at the equilibrium vapor pressure p_1 of the bulk liquid, is subjected to a sudden expansion. From resistance thermometry of these sudden expansions using the inert carrier gas only [e.g., Makower 1903] it is known that they are reversible¹ and that they are also adiabatic in sufficiently large chambers. Furthermore Volmer and Flood [1934] have shown from oscilloscope traces of a resistance thermometer that the duration of the theoretical terminal temperature is several tenths of a second for expansion ratios V_2/V_1 less than about 1.4 (corresponding to a temperature drop of about 30 °C) in a chamber of one liter volume. For a larger volume and faster piston speeds than used by Volmer and Flood, the duration of the theoretical terminal temperature should be appreciable for even larger expansion ratios. One notes that the expansions may be accomplished without a piston by merely opening a valve to an evacuated vessel; however such expansions may not be sufficiently fast to reach the theoretical terminal temperature.

The terminal temperature of a reversible adiabatic expansion of an ideal gas is given by

$$T_2 = T_1 \left(\frac{V_2}{V_1} \right)^{1-\nu} \quad (1)$$

in which ν is the ratio of specific heats of the gaseous mixture at constant pressure and volume, respectively. If p_∞ denotes the equilibrium vapor pressure of the bulk liquid at T_2 , the supersaturation ratio is

$$\frac{p}{p_\infty} = \frac{p_1}{p_\infty} \frac{V_1}{V_2} \frac{T_2}{T_1}, \quad (2)$$

upon the excellent assumption that the mixture behaves as an ideal gas. In the usual technique,

several preliminary expansions are made to create droplets on the dust particles so that they will fall to the bottom of the chamber and thus be removed. Then the expansion ratio is increased in successive expansions. For the case of water vapor in air, Wilson [1897, 1898, 1899] and others have found that nothing happens on increasing the expansion ratio until a supersaturation ratio of 4.2 [at 267 K] is reached, whereupon a rain-like precipitation occurs on the natural stationary concentration [$\sim 10^3/\text{cm}^3$] of negative ions in the air-vapor mixture (the negative ion limit). Then there is no further appreciable increase in the amount of precipitation until a supersaturation of 8.0 [at 257 K] where a dense fog, containing of the order of 10^6 droplets per cm^3 , is formed by homogeneous nucleation (the fog limit). In the presence of an appropriate electric field, Wilson [1899] could detect the positive ion limit at a supersaturation ratio of about six.

Volmer and Flood [1934] and others used an electric field, which supposedly removed almost all of the ions. They claimed that homogeneous nucleation actually began only slightly above the negative ion limit at a supersaturation ratio of 5.0 [at 260 K], and they took this homogeneous "rain limit", which they thought corresponded to a nucleation rate of about $1 \text{ cm}^{-3} \text{ s}^{-1}$, as their criterion for the critical supersaturation. They believed that the concentration of droplets does not increase rapidly until the fog limit because the supersaturation is relieved due to consumption of monomer and warming by the heat of condensation.

An alternative point of view, as expressed for example by Hirth and Pound [1963], is that this homogeneous rain limit actually represents nucleation on an attenuated (by the field) concentration of ions. However, as will be discussed in a later section, the diffusion cloud chamber, when used with an electric field, apparently can separate the effect of ions from homogeneous nucleation effects, and the homogeneous rain limit is verified. Also no existing theory of homogeneous nucleation can account for the paucity of condensation below the Wilson fog limit, unless it is brought about by one of the uncontrolled experimental conditions mentioned above. Therefore it will be assumed in this paper that the absence of homogeneous nucleation noted by Wilson below the fog limit is an experimental artifact of the expansion cloud chamber method. If it is not, then all of the data in the accompanying tables and graphs which purport to describe small homogeneous nucleation rates ($\sim 10^2 \text{ cm}^{-3} \text{ s}^{-1}$ or less) just above the ion limit may be wrong.

2.2. The Supersonic Nozzle

The supersonic nozzle technique for accomplishing adiabatic expansions was adapted for homoge-

¹ The reversibility is an expected result in view of the high thermal velocity of gas molecules with respect to the speed of the piston.

neous nucleation studies by Wegener and Mack [1958], Wegener and Pouring [1964], Hill [1966] and Duff and Hill [1966]. The speed of the reversible adiabatic expansion is sufficiently great that much higher maximum critical supersaturations can be observed than in expansion cloud chambers, and peak nucleation rates may reach 10^{12} to 10^{18} cm^{-3} s^{-1} for short periods of time. Thus ions or dust particles, in the usual relatively small concentrations, are unimportant as agents for condensation. On the other hand, the expansion speed is not so high that transient effects are important; enough time (~ 20 μs) is available to establish the stationary concentration distribution of embryos for nucleation. Another great advantage of the supersonic nozzle is that the flow conditions are nearly stationary and thus the history of the entire expansion is readily observed. Further, the wall boundary layers are thin relative to the nozzle diameter, and contamination and heating from the walls are thereby avoided. Nucleation is unlikely to occur in the boundary layers because these are generally superheated. The stream expanding between the wall boundary layers may be taken as a uniform adiabatic flow. The condensate particles occupy only a very small volume, and, because they are less than 1000 \AA in diameter, travel with the bulk velocity of the stream.

The rate of condensation may be inferred directly from measurements of the wall static pressure distribution. The point at which the static pressure deviates by about 1 percent from the "dry" pressure distribution is taken as the location of the onset of condensation. Wegener and Stein [1967] studied the Rayleigh scattering of a helium-neon laser beam by the resultant water fog in a supersonic nozzle and found a concentration of some 10^{12} droplets cm^{-3} of about 40 \AA in radius, consistent with a nucleation rate of $\sim 10^{15}$ cm^{-3} s^{-1} .

Actually, in the later, more sophisticated work cited above, mass, momentum and energy balances and the growth rate equation are applied to the stream, together with an assumed nucleation rate expression, to reproduce the observed pressure distribution. This complicated calculation is generally done with the aid of a computer. In this connection, one notes that the condensation zone is always located well downstream of the throat to facilitate calculation of the corresponding theoretical pressure distribution. A fit of the calculated to the observed pressure distribution yields the correct nucleation rate expression and an estimate of the effective condensation coefficient. The resultant nucleation rates turn out to be of the order of 10^{12} – 10^{18} cm^{-3} s^{-1} at the incidence of condensation.

2.3. The Diffusion Cloud Chamber

The diffusion cloud chamber technique was adapted for nucleation studies by Franck and Hertz [1956], Hertz [1956] and Katz and Ostermier [1967]. In this stationary-state device an adiabatic expansion is not used to produce the supersaturation. Rather, the supersaturation is produced in a diffusing stream of vapor with a temperature gradient parallel to the axis of diffusion. Since the equilibrium vapor pressure of the bulk liquid is exponential with temperature and the dependence of partial pressure on temperature is linear, a fairly large supersaturation may be produced in the chamber. In practice, a short cylinder of large diameter is used to minimize convection and wall effects, and the liquid is evaporated from a pool on the warm flat floor and condensed on the cool flat ceiling. The liquid then drains down the walls to the pool on the bottom. A light carrier gas, usually hydrogen or helium, is used so that the density of the gaseous mixture decreases from bottom to top of the cylinder, thus avoiding convection.

No instruments for measuring temperature or pressure can be placed in the volume of the chamber, because nucleation and condensation would occur on them, thus relieving the supersaturation and perturbing the conditions in the chamber. Rather, the stationary conditions in the chamber must be calculated from a knowledge of the boundary conditions in this one dimensional diffusion and heat transfer problem. These boundary conditions are the temperatures of the liquid surfaces on the lower and upper plates and the vapor pressures corresponding to these temperatures. The temperatures are measured by thermocouples which are usually embedded in the surfaces of the metal plates, and estimation of the liquid surface temperature from these thermocouple readings is a major experimental problem. Assuming that the surface temperatures are correct, the temperature and partial pressure profiles and hence the supersaturation profile along the axis of the cylinder can be calculated. The coupling of currents of matter and heat is duly considered, and this complicated calculation is customarily performed on a computer.

The "critical condition" of the cloud chamber is determined by slowly raising the temperature of the lower plate until droplets are just observed to form (at a rate of about 1 cm^{-3} s^{-1}) at a certain level in the chamber. The height of this level is not taken as a measurement, because its value is too imprecise. Rather, the supersaturation profile is computed for this set of experimental conditions. Similar critical conditions and supersaturation profiles are determined for other values of temperature of the top plate. Each of these supersaturation pro-

files (called envelopes) are plotted against temperature, and the curve tangent to this series of envelopes is the experimental curve of critical supersaturation versus temperature.

In the absence of an electric field, the critical supersaturation so determined is for nucleation on the natural, stationary concentration of ions (which is appreciably less for a hydrogen or helium carrier gas than the $\sim 10^3$ ion pairs present when air is the carrier). When an electric field is used to remove the ions, the only ion condensation appears as a trail of drops formed on the trail of ions left by energetic particles. The critical condition of the chamber is then reached only at some higher supersaturation supposedly characteristic of homogeneous nucleation; increase of the supersaturation beyond this point is said to be accompanied by a sharp increase in the concentration of droplets.

3. Criteria for Inclusion of Data in Tables and Graphs

In regard to the expansion cloud chamber method, the following conditions had to be satisfied to warrant inclusion of the data in the tables:

- (a) Essential adiabaticity and reversibility of the expansions such that the terminal temperature was surely attained for a sufficient period of time.
- (b) Inappreciable heating by condensation such that the terminal temperature was surely attained for a sufficient period of time.
- (c) Inappreciable consumption of monomer during the nucleation period.
- (d) Inappreciable evaporation of bulk liquid in the chamber during expansion.
- (e) Sufficiently precise measurements of temperature, pressure and volume.
- (f) Sufficiently pure liquids.
- (g) Absence of chemical reactions, e.g., reaction of vapor with the carrier gas.
- (h) Absence of important impurities and dust particles.
- (i) Absence of artificial radiation sources (especially in determinations of the ion limit), which produce unknown concentrations of unidentified ions.
- (j) Inappreciable coursening of condensed droplets (Ostwald ripening) as discussed by Feder et al. [1966] Such coursening would lead to a great decrease in droplet concentration.
- (k) No large uncertainty as to whether the nuclei are liquid or solid.

The above criteria were also used for the supersonic nozzle results, together with the requirement that the expansion not be too rapid for establishment of a stationary embryo concentration distribution.

For the diffusion cloud chamber data, the criteria numbered above were used with the exception of (a) and (d). Also (b) and (c) are replaced by:

- (b') Inappreciable heating by condensation in the volume of the chamber.
- (c') Inappreciable consumption of monomer by condensation in the volume of the chamber.

In addition, there had to be no evidence of appreciable convective effects.

Finally, the author particularly regrets that the results of Katz and Ostermier [1967] are not included in the present tables. Those results were calculated on the assumption of a linear dependence of the thermal conductivity of the gaseous mixture on composition. He has been advised by Dr. Katz that subsequent investigation reveals that this assumption is sufficiently in error to require recalculation of the results from the raw data. The work is now in progress, and this valuable information should be forthcoming in the near future. A similar assumption was made in the work of Franck and Hertz [1956]; it is assumed that the corresponding errors are smaller in the case of their work.

4. The Tables and Graphs

The meaning of the tables and graphs is best understood by reference to the text.

It seems of prime importance to note the major inconsistencies, reservations and uncertainties:

- (a). The writer is unable to reproduce the critical supersaturations reported by Volmer and Flood [1934] and by Scharrer [1939] from their published expansion ratios (except for the case of water). This problem is difficult to resolve, because they are not sufficiently explicit as to their sources of vapor pressure data. In general, the writer's results are some one-half to one supersaturation ratio unit lower.
- (b). The results of Volmer and Flood [1934] and Scharrer [1939] for homogeneous nucleation of methanol (about 3.2 at 279 K) are at odds with the results of Franck and Hertz [1956], who found a critical supersaturation ratio of about 1.9 at 270 K. The former workers used the expansion cloud chamber method, while the latter authors used a diffusion cloud chamber. Both took the criterion for critical supersaturation to be a nucleation rate of about $1 \text{ cm}^{-3} \text{ s}^{-1}$. Franck and Hertz used hydrogen as the carrier gas, while the others used air.
- (c). As discussed in the description of the expansion cloud chamber, it is assumed in this paper that the absence of homogeneous nucleation noted by Wilson [1897] and Powell [1928] below the fog limit is an

experimental artifact of the expansion cloud chamber method. If it is not, then all of the data in the accompanying tables and graphs which purport to describe small homogeneous nucleation rates ($\sim 10^2 \text{ cm}^{-3} \text{ s}^{-1}$ or less) just above the ion limit may be wrong.

5. Conclusions to be Drawn from the Tables and Graphs

- (a). If the three exceptions noted above are overlooked, the three different experimental methods are in reasonable agreement for homogeneous nucleation of all substances. One notes that in order to compare the results for high homogeneous nucleation rates (i.e., the supersonic nozzle results and the expansion cloud chamber results of Wilson [1897] and Powell [1928]), with the other critical supersaturation data for low homogeneous nucleation rates, it is necessary to have recourse to a theoretical nucleation rate equation for the extrapolation. Although the theory is not discussed in this paper, it is found that a single nucleation-rate-equation-describes all observed rates for a given substance. The trouble is that different substances require different nucleation rate equations. (There now appear to be two principal theoretical rate equations.)
- (b). If exception (a) above is overlooked, then the critical supersaturation ratios for nucleation on a stationary concentration of natural ions are the same by either the expansion cloud chamber or diffusion cloud chamber method.
- (c). The critical supersaturation for nucleation on a natural stationary concentration of ions is only several tenths of a supersaturation ratio unit below that for a low rate of homogeneous nucleation ($\sim 1 \text{ cm}^{-3} \text{ s}^{-1}$).

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TABLE 1. Critical supersaturation ratios for homogeneous nucleation of liquids from the vapor

Substance	Purity	Electric field	Carrier gas	Purity of carrier gas	Carrier gas pressure	Temperature	Effective condensation coefficient	Critical supersaturation	Method	Authors
Ammonia	<30ppm H ₂ O (Sometimes treated with sodium with no change in results)	None	Air	Compressed (oil-free), filtered, and dehumidified, <0.03ppm H ₂ O (Varied to >0.03ppm with no change in results for low H ₂ O contents)	~ 1 Atm	185-200 K	Not estimated	~ 3.5 (see Fig. 1), Corresponding to a Rate of ~ 10 ¹⁵ cm ⁻³ s ⁻¹	Supersonic Nozzle	Jaeger et al. [1969]
Ammonia	<30ppm H ₂ O	None	None		None	220-245 K	Not estimated	~ 2.0 (see Fig. 1), Corresponding to a Rate of ~ 10 ¹⁵ cm ⁻³ s ⁻¹	Supersonic Nozzle	Kremmer and Okorounnu [1965]
Benzene (C ₆ H ₆)	Unstated	None	Air	Compressed (oil-free), filtered, and dehumidified, <0.03 ppm H ₂ O (Varied H ₂ O content to >0.03ppm with no change in results)	~ 1 Atm	190-227 K	~ 0.1	~ 33 at 227 K (see Fig. 2), Corresponding to a Rate of ~ 10 ¹⁵ cm ⁻³ s ⁻¹	Supersonic Nozzle	Dawson et al. [1969]
Benzene	Kahlbaum's distilled and dried	Of unstated strength	Air	Cleaned by repeated expansions	~ 1 Atm.	254 K		5.3 ± 0.1, ^{a,c} Corresponding to a Rate of ~ 1 cm ⁻³ s ⁻¹ ^b	Expansion cloud chamber	Scharrer [1939]
Carbon tetrachloride	Kahlbaum's, distilled and dried	Of unstated strength	Air.	Cleaned by repeated expansions	~ 1 Atm	246 K		6.5 ± 0.01 ^{a,c} Corresponding to a Rate of ~ 1 cm ⁻³ s ⁻¹ ^b	Expansion cloud chamber	Scharrer [1939]
Chlorobenzene	Kahlbaum's, distilled and dried	Of unstated strength	Air	Cleaned by repeated expansions	~ 1 Atm	250 K		9.5 ± 0.1, ^{a,c} corresponding to a rate of ~ 1 cm ⁻³ s ⁻¹ ^b	Expansion cloud chamber	Scharrer [1939]
Chloroform (CHCl ₃)	Unstated	None	Air	Compressed (oil-free), filtered, and dehumidified, < 0.03ppm H ₂ O (varied H ₂ O content to > 0.03ppm with no change in results)	~ 1/3 Atm	195-229 K	~ 1	~ 40 to 15 (See Fig. 3), corresponding to a rate of ~ 10 ¹⁵ cm ⁻³ s ⁻¹	Supersonic nozzle	Dawson et al. [1969]
Chloroform (CHCl ₃)	Kahlbaum's distilled and dried	Of unstated strength	Air	Cleaned by repeated expansions	~ 1 Atm	258 K		3.7 ± 0.1, ^{a,c} corresponding to a rate of ~ 1 cm ⁻³ s ⁻¹ ^b	Expansion cloud chamber	Scharrer [1939]

TABLE 1. Critical supersaturation ratios for homogeneous nucleation of liquids from the vapor—Continued

Substance	Purity	Electric field	Carrier gas	Purity of carrier gas	Carrier gas pressure	Temperature	Effective condensation coefficient	Critical supersaturation	Method	Authors
Ethanol	"Absolute" alcohol. Distilled and boiled under vacuum to remove	50 volts/cm	Hydrogen	Electrolytic, not further purified	~ 1 Atm and ~ 1/3 Atm	250–280 K		3.0 to 1.9 ± 0.1 (See table 2), corresponding to a rate of ~ 1 cm ⁻³ s ⁻¹	Diffusion cloud chamber	Franck and Hertz [1956]
Ethanol	Kahlbaum's distilled and dried	Of unstated strength	Air	Cleaned by repeated expansions	~ 1 Atm	275 K		2.1 ± 0.1, ^a corresponding to a rate of ~ 1 cm ⁻³ s ^{-1b}	Expansion cloud chamber	Scharrer [1939]
Ethanol	Distilled over CaO while being bubbled with H ₂	~ 25 volts/cm	Air	Cleaned by repeated expansions	~ 1 Atm	273.2 K		2.3 ± 0.1, ^a corresponding to a rate of ~ 1 cm ⁻³ s ^{-1b}	Expansion cloud chamber	Volmer and Flood [1934]
Freon (CCl ₃ F)	Unstated	None	Air	Compressed (oil-free), filtered, and dehumidified, < 0.03ppm H ₂ O (varied H ₂ O content to > 0.03ppm with no change in results)	~ 1/3 Atm	160–175 K	~ 0.1	~ 67 at 175 K (See Fig. 4), corresponding to a rate of ~ 10 ¹⁵ cm ⁻³ s ⁻¹	Supersonic nozzle	Dawson et al. [1969]
Iso-propyl alcohol	"Kahlbaum's purest", Distilled over CaO	~ 25 volts/cm	Air	Cleaned by repeated expansions	~ 1 Atm	264.7 K		2.80 ± 0.1, ^a corresponding to a Rate of ~ 1 cm ⁻³ s ^{-1b}	Expansion cloud chamber	Volmer and Flood [1934]
Methanol	Merck analytical grade	50 volts/cm	Hydrogen	Electrolytic, not further purified	~ 1 Atm and ~ 1/3 Atm	244–278 K		2.4 to 1.8 ± 0.1 (See table 3), Corresponding to a Rate of ~ 1 cm ⁻³ s ⁻¹	Diffusion cloud chamber	Franck and Hertz [1956]
Methanol	Kahlbaum's, distilled and dried	Of unstated strength	Air	Cleaned by repeated expansions	~ 1 Atm	264 K		3.5 ± 0.1, ^a corresponding to a Rate of ~ 1 cm ⁻³ s ^{-1b}	Expansion cloud chamber	Sharrer [1939]
Methanol	Distilled over CaO while being bubbled with H ₂	~ 25 volts/cm	Air	Cleaned by repeated expansions	~ 1 Atm	270.0 K		3.2 ± 0.01, ^a corresponding to a Rate of ~ 1 cm ⁻³ s ^{-1b}	Expansion cloud chamber	Volmer and Flood [1934]
n-Butyl alcohol	"Kahlbaum's purest", distilled over CaO	~ 25 volts/cm	Air	Cleaned by repeated expansions	~ 1 Atm	270.2 K		4.6 ± 0.1, ^a corresponding to a Rate of ~ 1 cm ⁻³ s ^{-1b}	Expansion cloud chamber	Volmer and Flood [1934]
n-Propyl alcohol	"Kahlbaum's purest", Distilled over CaO	~ 25 volts/cm	Air	Cleaned by repeated expansions	~ 1 Atm	270.4 K		3.05 ± 0.1, ^a corresponding to a Rate of ~ 1 cm ⁻³ s ^{-1b}	Expansion cloud chamber	Volmer and Flood [1934]
Nitromethane	Washed with salt water, dried with P ₂ O ₅	~ 25 volts/cm	Air	Cleaned by repeated expansions	~ 1 Atm	252.2 K		6.05 ± 0.1, ^a corresponding to a Rate of ~ 1 cm ⁻³ s ^{-1b}	Expansion cloud chamber	Volmer and Flood [1934]

TABLE 1. Critical supersaturation ratios for homogeneous nucleation of liquids from the vapor—Continued

Substance	Purity	Electric field strength	Carrier gas	Purity of carrier gas	Carrier gas pressure	Temperature	Effective condensation coefficient	Critical supersaturation	Method	Authors
Water	Unstated	Of unstated strength	Air	Cleaned by repeated expansions	~1 Atm	264 K		4.9 ± 0.1 , corresponding to a rate of $\sim 1 \text{ cm}^{-3} \text{ s}^{-1b}$	Expansion cloud chamber	Scharrer [1939]
Water	Distilled and boiled	With (400 volts/cm) and without	Air, O ₂ , N ₂ , H ₂	Cleaned by repeated expansions	~1 Atm	257.3 K		7.9 ± 0.1 , corresponding to a rate of $\sim 10^8 \text{ cm}^{-3} \text{ s}^{-1}$ [See Feder et al., 1956]	Expansion cloud chamber	Wilson [1897] [1899]
Water	Unstated	None	Air	Cleaned by repeated expansions	~1 Atm	246.7–320.1 K		$8.95 - 2.97 \pm 0.1$, (See Fig. 5), corresponding to a rate of $\sim 10^8 \text{ cm}^{-3} \text{ s}^{-1}$ (See Feder et al. 1956)	Expansion cloud chamber	Powell [1928]
Water	Unstated	~25 volts/cm	Air	Cleaned by repeated expansions	~1 Atm	260 and 275 K		5.0 and 4.2 ± 0.1 , corresponding to a rate of $\sim 1 \text{ cm}^{-3} \text{ s}^{-1b}$	Expansion cloud chamber	Volmer and Flood [1934]
Water	Unstated	None	None			285–360 K	Not estimated	~14 to 3.4 (See Fig. 6), corresponding to a rate of $\sim 10^{15} \text{ cm}^{-3} \text{ s}^{-1}$	Supersonic nozzle	Yellot [1934]
Water	Unstated	None	None			345–365 K	Not estimated	~4.0 (See Fig. 6), corresponding to a rate of $\sim 10^{18} \text{ cm}^{-3} \text{ s}^{-1}$	Supersonic nozzle	Retallata [1936]
Water	Unstated	None	None			295–320 K	Not estimated	~5.8 (See Fig. 6), corresponding to a rate of $\sim 10^{18} \text{ cm}^{-3} \text{ s}^{-1}$	Supersonic nozzle	Binnie and Wood [1938]
Water	Unstated	None	None			285–305 K	Not estimated	~6.7 (See Fig. 6), corresponding to a rate of $\sim 10^{15} \text{ cm}^{-3} \text{ s}^{-1}$	Supersonic nozzle	Binnie and Green [1942]
Water	Unstated	None	Air	Unstated	~1 Atm	200–220 K	~0.25	(See Fig. 6) Perhaps the nuclei were ice	Supersonic nozzle	Wegener and Pouring [1964]
Water	Unstated	None	None			265–335 K	Not estimated	~18 to 4.2 (See Fig. 6), corresponding to a rate of $\sim 10^{15} \text{ cm}^{-3} \text{ s}^{-1}$	Supersonic nozzle	Gyarmathy and Meyer [1965]
Water	Unstated	None	Air	Compressed (oil-free), filtered, and dehumidified, <0.03ppm H ₂ O	~1 Atm	220–260 K	~0.1	~100 to 15 (See Fig. 6), corresponding to a rate of $\sim 10^{11} \text{ cm}^{-3} \text{ s}^{-1}$	Supersonic nozzle	Jaeger et al. [1969]

TABLE 1. Critical supersaturation ratios for homogeneous nucleation of liquids from the vapor—Continued

Substance	Purity	Electric field	Carrier gas	Purity of carrier gas	Carrier gas pressure	Temperature	Effective condensation coefficient	Critical supersaturation	Method	Authors
Water-ethanol	Ethanol distilled over CaO while being bubbled with H ₂ . Purity of water unstated	~ 25 volts/cm	Air	Cleaned by repeated expansions	~ 1 Atm	264-280-273 K		4.8-1.8-2.3±0.1 (See Table IV and Fig. 7), corresponding to a rate of ~ 1 cm ⁻³ s ^{-1b}	Expansion cloud chamber	Flood [1934]

^a The writer is unable to arrive at these critical supersaturations when he uses the published expansion data and standard vapor pressure data (e.g. from the International Critical Tables).
^b Feder et al (1966), on the basis of heat-transfer considerations, estimate the actual rate to have been of the order of 10² cc⁻¹ sec⁻¹.

^c The adiabaticity at this high expansion ratio is questioned. Such an error would tend to make the observed critical supersaturation higher than the true value.

TABLE 2. Critical supersaturation ratios for homogeneous nucleation of liquid from ethanol vapor in a diffusion cloud chamber [After Franck and Hertz, 1956]

Temperature	Critical supersaturation for a carrier gas pressure of ~ 1 atm	Critical supersaturation for a carrier gas pressure of $\sim 1/3$ atm
<i>K</i>		
280	1.96 ± 0.1	1.88 ± 0.1
277	2.02 ± 0.1	1.94 ± 0.1
273	2.10 ± 0.1	2.02 ± 0.1
270	2.18 ± 0.1	2.10 ± 0.1
267	2.26 ± 0.1	2.17 ± 0.1
263	2.39 ± 0.1	2.29 ± 0.1
260	2.51 ± 0.1	2.38 ± 0.1
255	2.76 ± 0.1	2.57 ± 0.1
250	3.06 ± 0.1	2.77 ± 0.1
245		2.99 ± 0.1
240		3.24 ± 0.1

TABLE 3. Critical supersaturation ratios for homogeneous nucleation of liquid from methanol vapor in a diffusion cloud chamber [After Franck and Hertz, 1956]

Temperature	Critical supersaturation for a carrier gas pressure of ~ 1 atm	Critical supersaturation for a carrier gas pressure of $\sim 1/3$ atm
<i>K</i>		
278	1.82 ± 0.1	1.80 ± 0.1
273	1.86 ± 0.1	1.84 ± 0.1
270	1.89 ± 0.1	1.87 ± 0.1
265	1.96 ± 0.1	1.92 ± 0.1
260	2.02 ± 0.1	1.98 ± 0.1
256	2.10 ± 0.1	2.05 ± 0.1
250	2.26 ± 0.1	2.17 ± 0.1
244	2.44 ± 0.1	2.30 ± 0.1
240		2.40 ± 0.1

TABLE 4. Critical supersaturation ratios for homogeneous nucleation of liquid from water-ethanol vapors in an expansion cloud chamber [After Flood, 1934]

Mole per cent ethanol in liquid	Temperature K	Mole per cent ethanol in nucleus	Critical supersaturation
0	263.7	0	4.85 ± 0.1
3.86	272.8	.8	$2.64 \pm .1$
11.5	275.6	3.7	$1.97 \pm .1$
35.3	280.4	8.5	$1.75 \pm .1$
67.1	277.0	25.0	$1.62 \pm .1$
77.9	274.9	61.0	$1.77 \pm .1$
90.3	273.8	82.0	$2.07 \pm .1$
100.0	273.2	100.0	$2.34 \pm .1$

TABLE 5. Critical supersaturation ratios for heterogeneous nucleation of liquids from the vapor on gaseous ions

Substance	Purity	Carrier gas	Purity of carrier gas	Carrier gas pressure	Charge of ions	Nature of ions	Electric field	Temperature	Critical supersaturation	Method	Authors
Benzene	Kahlbaum's distilled and dried	Air	Cleaned by repeated expansions	~ 1 Atm	+ and -	Stationary concentration in the gaseous mixture, ~ $10^9/\text{cm}^3$ [See Volmer, 1939]	None	254 K	5.4 ± 0.1 , ^{a,d} corresponding to a rate of ~ $1 \text{ cm}^{-3} \text{ s}^{-1b}$	Expansion cloud chamber	Scharrer [1939]
Carbon tetrachloride	Kahlbaum's, distilled and dried	Air	Cleaned by repeated expansions	~ 1 Atm	+ and -	Stationary concentration in the gaseous mixture, ~ $10^9/\text{cm}^3$ [See Volmer, 1939]	None	247 K	5.7 ± 0.1 , ^{a,d} corresponding to a rate of ~ $1 \text{ cm}^{-3} \text{ s}^{-1b}$	Expansion cloud chamber	Scharrer [1939]
Chlorobenzene	Kahlbaum's, distilled and dried	Air	Cleaned by repeated expansions	~ 1 Atm	+ and -	Stationary concentration in the gaseous mixture, ~ $10^9/\text{cm}^3$ [See Volmer, 1939]	None	252 K	8.7 ± 0.1 , ^{a,d} corresponding to a rate of ~ $1 \text{ cm}^{-3} \text{ s}^{-1b}$	Expansion cloud chamber	Scharrer [1939]
Chloroform	Kahlbaum's, distilled and dried	Air	Cleaned by repeated expansions	~ 1 Atm	+ and -	Stationary concentration in the gaseous mixture, ~ $10^9/\text{cm}^3$ [See Volmer, 1939]	None	260 K	3.4 ± 0.1 , ^d corresponding to a rate of ~ $1 \text{ cm}^{-3} \text{ s}^{-1b}$	Expansion cloud chamber	Scharrer [1939]
Ethanol	Kahlbaum's, distilled and dried	Air	Cleaned by repeated expansions	~ 1 Atm	+ and -	Stationary concentration in the gaseous mixture, ~ $10^9/\text{cm}^3$ [See Volmer, 1939]	None	276 K	2.1 ± 0.1 , ^d corresponding to a rate of ~ $1 \text{ cm}^{-3} \text{ s}^{-1b}$	Expansion cloud chamber	Scharrer [1939]
Ethanol	Unstated	H ₂ , He	Electrolytic H ₂ , not further purified. He purity unstated.	~ 1 Atm	+ and -	Stationary concentration in the gaseous mixture, ~ $10^9/\text{cm}^3$. [See Volmer, 1939].	None	264, 269 and 275 K.	2.2, 2.0 and 1.9 ± 0.1 , corresponding to a rate of $0.1 \text{ cm}^{-3} \text{ s}^{-1}$.	Diffusion cloud chamber.	Hertz [1956].
Methanol	Kahlbaum's, distilled and dried.	Air	Cleaned by repeated expansions.	~ 1 Atm	+ and -	Stationary concentration in the gaseous mixture, ~ $10^9/\text{cm}^3$. [See Volmer, 1939].	None	266 K	3.2 ± 0.1 , ^d corresponding to a rate of ~ $1 \text{ cm}^{-3} \text{ s}^{-1b}$.	Expansion cloud chamber.	Scharrer [1939]
Methanol	Merck analytical grade.	H ₂ , He	Electrolytic H ₂ , not further purified. He purity unstated.	~ 1 Atm	+ and -	Stationary concentration in the gaseous mixture, ~ $10^9/\text{cm}^3$. [See Volmer, 1939].	None	264, 270 and 276 K.	1.85, 1.8 and 1.75 ± 0.1 , corresponding to a rate of ~ $0.1 \text{ cm}^{-3} \text{ s}^{-1}$.	Diffusion cloud chamber.	Hertz [1956].
Water	Distilled and boiled.	Air	Cleaned by repeated expansions.	~ 1 Atm	+ and -	Stationary concentration in the gaseous mixture, ~ $10^9/\text{cm}^3$. [See Volmer, 1939]. ^c	None	263.1, 267.3 and 275.3 K.	4.4, 4.2 and 4.0 ± 0.1 , corresponding to a rate of ~ $1 \text{ cm}^{-3} \text{ s}^{-1b}$	Expansion cloud chamber.	Wilson [1897], [1898].

TABLE 5. Critical supersaturation ratios for heterogeneous nucleation of liquids from the vapor on gaseous ions — Continued

Substance	Purity	Carrier gas	Purity of carrier gas	Carrier gas pressure	Charge of ions	Nature of ions	Electric field	Temperature	Critical supersaturation	Method	Authors
Water	Distilled and boiled.	O ₂	Cleaned by repeated expansions.	~1 Atm	+ and —	Stationary concentration in the gaseous mixture, ~10 ³ /cm ³ . [See Volmer, 1939]. ^c	None	266.9 K	4.3 ± 0.1, corresponding to a rate of ~1 cm ⁻³ s ^{-1b} .	Expansion cloud chamber.	Wilson [1897], [1898].
Water	Distilled and boiled.	N ₂	Cleaned by repeated expansions.	~1 Atm	+ and —	Stationary concentration in the gaseous mixture, ~10 ³ /cm ³ . [See Volmer, 1939]. ^c	None	266.4 K	4.4 ± 0.1, corresponding to a rate of ~1 cm ⁻³ s ^{-1b} .	Expansion cloud chamber.	Wilson [1897], [1898].
Water	Unstated	Air	Cleaned by repeated expansions.	~1 Atm	+ and —	Stationary concentration in the gaseous mixture, ~10 ³ /cm ³ . [See Volmer, 1939]. ^c	None	266.6–323.6 K.	4.0–2.5 ± 0.1 [See Fig. 5], corresponding to a rate of ~1 cm ⁻³ s ^{-1b} .	Expansion cloud chamber.	Powell [1928].
Water	Unstated	Air	Cleaned by repeated expansions.	~1 Atm	+ and —	Stationary concentration in the gaseous mixture, ~10 ³ /cm ³ . [See Volmer, 1939]. ^c	None	277.0 to 262.8 K.	3.9–4.2 ± 0.1, [See Table 6], corresponding to a rate of ~1 cm ⁻³ s ^{-1b} .	Expansion cloud chamber.	Volmer and Flood [1934].
Water	Unstated	Air	Cleaned by repeated expansions.	~1 Atm	+ and —	Stationary concentration in the gaseous mixture, ~10 ³ /cm ³ . [See Volmer, 1939]. ^c	None	265 K	4.7 ± 0.1, corresponding to a rate of ~1 cm ⁻³ s ^{-1b} .	Expansion cloud chamber.	Scharrer [1939].

^a The adiabaticity at this high expansion ratio is questioned. Such an error would tend to make the observed critical supersaturation higher than the true value.

^b Feder et al. [1966], on the basis of heat-transfer considerations, estimate the actual rate to have been of the order of 10² cm⁻³ s⁻¹.

^c Actually, the negative ions are the ones that are operative in producing nucleation of water at this supersaturation [Wilson, 1899].

^d The writer is unable to arrive at these critical supersaturations when he uses the published expansion data and standard vapor pressure data [e.g., from the International Critical Tables].

TABLE 6. Critical supersaturation ratios for heterogeneous nucleation of liquid from water vapor on the natural stationary concentration of ions in a vapor-air mixture in an expansion cloud chamber (After Volmer and Flood, 1934)

Temperature	Critical supersaturation
<i>K</i>	
277.0	3.9 ± 0.1
276.8	3.9 ± 0.1
275.3	3.8 ± 0.1
263.7	4.3 ± 0.1
263.5	4.2 ± 0.1
262.7	4.2 ± 0.1
262.8	4.2 ± 0.1

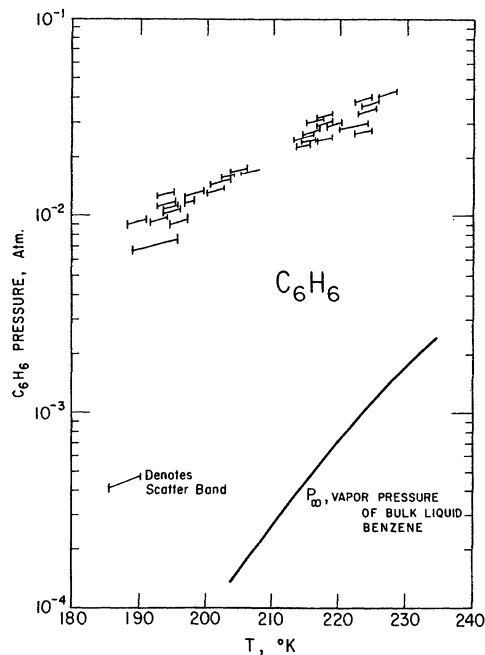


FIGURE 2. Critical pressure of benzene vapor for homogeneous nucleation in supersonic nozzles. (after Dawson et al., 1969)

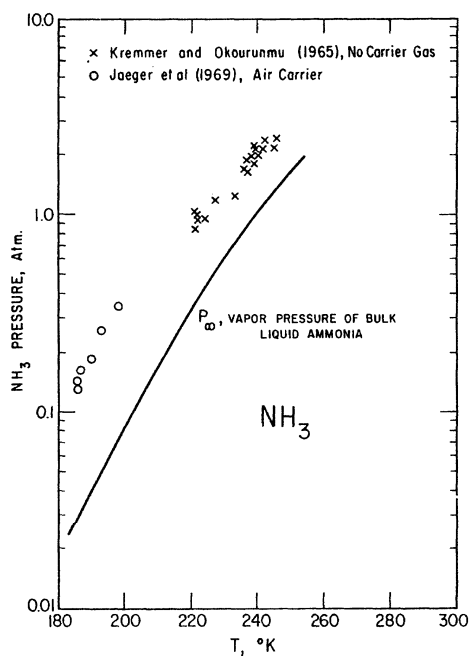


FIGURE 1. Critical pressure of ammonia vapor for homogeneous nucleation in supersonic nozzles. (After Jaeger et al., 1969)

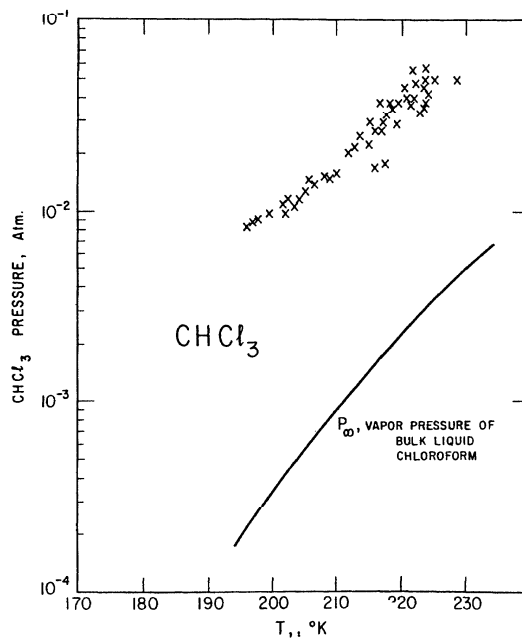


FIGURE 3. Critical pressure of chloroform vapor for homogeneous nucleation in supersonic nozzles. (After Dawson et al., 1969)

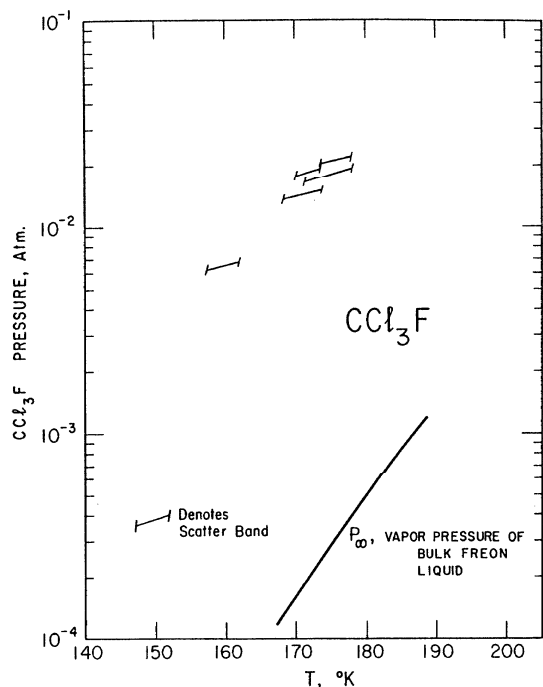


FIGURE 4. Critical pressure of freon vapor for homogeneous nucleation in supersonic nozzles. (After Dawson et al., 1969)

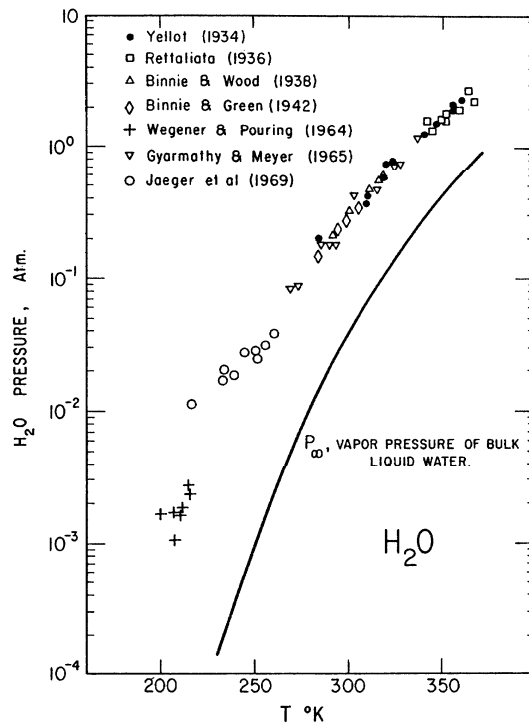


FIGURE 6. Critical pressure of water vapor for homogeneous nucleation in supersonic nozzles. (After Jaeger et al., 1969)

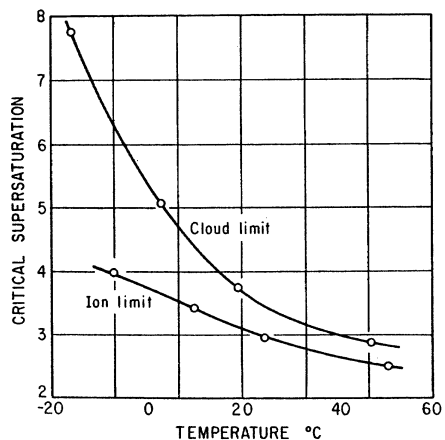


FIGURE 5. Critical supersaturation ratios for homogeneous nucleation, upper curve, of liquid from water vapor in an expansion cloud chamber. (After Powell, 1928)

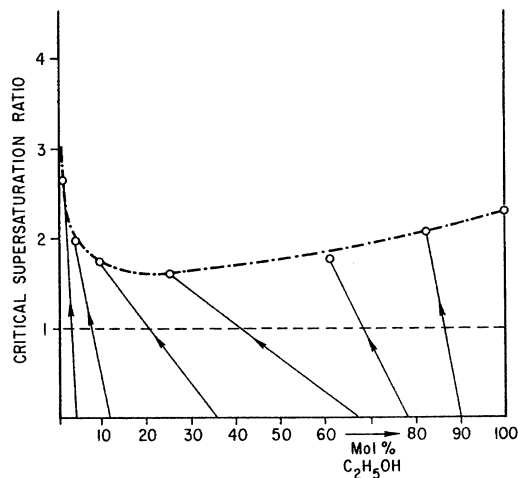


FIGURE 7. Critical supersaturation ratios for homogeneous nucleation of liquid from water-ethanol vapors. (After Flood, 1934)