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The Spontaneous Condensation of Vapour and the Formation of Condensation Aerosols

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The development of the theory of spontaneous condensation of vapour, experimental studies of this phenomenon, and the use of the theoretical results for calculations on the formation of condensation aerosols are reviewed. The difficulty of calculating the free energy of formation of the nuclei of a new phase is examined in detail, and particular attention is paid to the problem of the contribution made by external degrees of freedom to the free energy. The problem of the existence of limiting supersaturation is discussed. Existing methods for the study of spontaneous condensation and the results obtained by these methods are examined critically. The bibliography contains 191 references.

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I. INTRODUCTION

The spontaneous (homogeneous) condensation of vapour, first examined at an early date by Gibbs, has recently been attracting increasing attention from specialists working in various fields of science and technology. Spontaneous condensation takes place in various important technological processes, in powder and vacuum metallurgy, in rocket jets, and in supersonic aerodynamic nozzles. The results obtained in the study of the condensation of vapour are important for an understanding of the mechanism of other first-order phase changes taking place in the solidification of alloys, boiling, cavitation, the crystallisation of polymers, the devitrification of glasses, and the separation of phases on a spinodal; the results are also important for the theory of the equation of state of gases. The number of papers devoted to this problem is increasing, and there is also an increase in the number of different views regarding fundamental problems of the theory, such as the determination of the free energy of nucleus formation, the accomodation of molecules on the surface of the nuclei, and the influence of the association of the condensing vapour. Reviews on this problem, published chiefly in other countries, generally do not deal objectively with some aspects. In the last two decades, new experimental methods for studying spontaneous condensation have appeared, but the results of these studies have been inadequately dealt with in the review literature. At the same time, experimental practice is requiring the development of theoretical methods of calculation which will make it possible to predict the course of the production of the particle distribution with respect to dimensions in condensation aerosols, since it is only when such methods have been developed that deliberate control of this process will be possible. The present review is devoted to a critical examination of modern theories of spontaneous condensation, experimental methods of study, the relationship between theory and experiment, and methods for calculating the microscopic model of aerosol formation.

II. THE PRESENT STUDY OF THE THEORY OF SPONTANEOUS CONDENSATION

The theory of spontaneous nucleus formation in a supersaturated vapour, developed by Volmer[1], Farkas[2], Becker and Doring[3], and in its most elegant and complete form by Zel'dovich[4,5] and Frenkel'[6,7], has long since become classical, and has been described in many reviews and monographs[8-10]. This theory is based on the model first proposed by Szilard and Farkas[2], according to which a supersaturated vapour consists of a mixture of single molecules and molecular aggregates (clusters), which, according to Frenkel', can be regarded as the nuclei of a new phase. In the present review the term "nucleus" will be used only to denote aggregates of supercritical dimensions, that is dimensions at which the aggregates are stable and the probability of their growth is greater than the probability of their volatilisation. According to the general theory of thermodynamic fluctuations, the number of aggregates decreases exponentially with increase in their free energy of formation ΔG. In an unsaturated vapour, the dependence of ΔG on the dimensions of the aggregate decreases monotonically, and in the supersaturated vapour it has a minimum corresponding to the dimensions of the critical cluster. In the classical theory we can express the probability $W_g(t)$ of finding a cluster at moment of time t at a certain point on the g axis (g is the number of molecules in the nucleus) by the equation for a Markovian process:

$$\frac{dW_g(t)}{dt} = \alpha_{g-1}W_{g-1}(t) - (\alpha_g + \beta_g)W_g(t) + \beta_{g+1}W_{g+1}(t) \qquad (1)$$

where α and β are the rate constants for the reactions $A_g + A_1 \rightarrow A_{g+1}$ and $A_{g+1} \rightarrow A_g + A_1$, and A_g and A_1 represent clusters consisting of g molecules and a single molecule. Under equilibrium conditions:

$$\beta_g = \alpha_{g-1}W^0_{g-1}/W^0_g \qquad (2)$$

where $W_g^0 = c_1 \exp(-\Delta G_g^0/kT)$, ΔG_g^0 is the equilibrium value of the free energy of formation of the aggregate, and c_1 the concentration of molecules. By substituting the values of W and β, and replacing the finite differences $\alpha_{g+1} - \alpha_g$ and $\beta_{g+1} - \beta_g$ by differentials, we transform Eqn. (1) into the form

$$\frac{\partial W(g,t)}{\partial t} = \frac{\partial}{\partial g}\left\{\alpha_g \frac{\partial W(g,t)}{\partial g} + \alpha_g \frac{W(g,t)}{kT}\frac{\partial(\Delta G_g)}{\partial g}\right\}. \quad (3)$$

This is essentially the Fokker–Planck equation for the diffusion of the aggregates along the g axis. It was first derived by Frenkel'. To determine the number of aggregates reaching supercritical dimensions in unit time, J, it is assumed that the process is a steady-state process, that is the quantity c_1 is kept constant, and the clusters are removed from the system when their dimensions exceed the critical dimensions g^*. We then have

$$\alpha_g \frac{\partial W(g)}{\partial g} + \alpha_g \frac{W(g)}{kT}\frac{\partial(\Delta G_g)}{\partial g} = -J. \quad (4)$$

Various authors have solved this equation and obtained a result which can be written in the general form:

$$J = 4\pi r^{*2}(p/\sqrt{2\pi mkT})\, c_1 Z \exp(-\Delta G^*/kT) \quad (5)$$

where $p/\sqrt{2\pi mkT}$ is the number of collisions undergone by the molecules of the vapour with unit area of the cluster surface, p the pressure and m the mass of a molecule of the vapour, and Z the non-equilibrium Zel'dovich factor—$Z = (\Delta G^*/3\pi kTg^{*2})^{1/2}$.

This factor is of the order of 10^{-1}–10^{-2} and characterises the deviation of the concentration of the clusters from the equilibrium value. Various expressions for J are given in the Table.

The equations given in the Table show that J depends to a marked extent on the magnitude of the supersaturation S. We can therefore speak of the "critical supersaturation", that is the supersaturation at which the rate of nucleus formation becomes appreciable. The critical supersaturation is usually taken to be that corresponding to a rate of formation of nuclei equal to 1 cm^{-3} s^{-1}. For water vapour saturated at room temperature, a change in supersaturation of 15% close to the critical value produces a change in J by a factor of $\sim 10^8$, and this makes it possible to find S_{cr} from comparatively rough determinations of the concentration of the aerosol produced in the experiment. Volmer and Flood[22] obtained for the magnitude of the critical supersaturation the expression

$$\lg S_{cr} = \sqrt{\frac{1{,}44}{\lg A}}\left(\frac{M}{\rho}\right)\left(\frac{\sigma}{T}\right)^3 \quad (6)$$

where A is the pre-exponential factor in Eqn. (5) for the rate of nucleus formation.

A key feature of the theory is the determination of the free energy of formation of the cluster. In the classical theory it is assumed that ΔG can be represented as the sum of two terms—a bulk term and a surface term:

$$\Delta G = Ag + Bg^{2/3} \quad (7)$$

where $A = kT\ln S$, $S = p/p_0$, p_0 is the equilibrium pressure of the vapour at the given temperature,

$$Bg^{2/3} = 4\pi r^2\sigma, \quad (8)$$

and σ is the surface tension, and it is assumed that the cluster has macroscopic values for the surface tension and the density ρ. This last assumption has been criticised many times. Attempts to calculate ΔG without apriori assumptions regarding the values of σ and ρ for the material of the nucleus can be divided into two main groups. In the first group, the authors have tried to express σ and ρ as functions of the dimensions of the nuclei, and in the second, various attempts have been made to calculate ΔG without the apriori assumption that this quantity can be divided into bulk and surface contributions.

Equations for the rate of nucleus formation*.

$J = a_c N^{4/3}(p/R)^2(2M\sigma/\pi)^{1/2}\exp[(-16\sigma^3M^2/3kp^2R^2T^2\ln^2 s)] \equiv \equiv A_\Phi \exp(-\Delta C_\Phi/kT) \equiv J_\Phi$	1, 5, 7, 12
$J = g^{*2/3}Z_\Phi$	3
$J = a_c(2M\sigma/N\pi)^{1/2}(p_0/kT)^2\rho^{-1}g^{*-2/3}\exp[(-\Delta H_\Phi/kT)(1-3g^{*-1/3}+2g^{-1*})]$	13
$J = A\exp[(-\Delta G_\Phi/kT)(1-2\sqrt[3]{4}g^{*-1/3}+4g^{*-1})]$	14
$J = a_c Np(2\pi MkT)^{-1/2}(4\pi d^2c^2)(kTN/\pi M)^{1/2}\exp(-\Delta C_\Phi/kT)$	11
$J = K\exp(-\Delta G_\Phi/kT)\sinh(-\alpha g^{*1/3}/3kT)$, $\alpha g^{*2/3} = 4\pi r^*\sigma$, K is a factor including the rate constant of the reaction, $A_g + A_1 \rightarrow A_{g+1}$	15
$J = J_\Phi/S$	16
$J = J_\Phi \cdot Q_t Q_r/c$	17
$J = J_\Phi Q_t Q_r (c_e/q_t)^2/c$	18
$J = J_\Phi (Q_t Q_r/c)(2\pi^* g)^{-1/2} e^{-\delta}$	19
$J = J_\Phi (Q_t Q_r/c)\, e^{\delta}(2\pi g^*)^{-1/2} S^{-1}$	20
$J = J_\Phi (Q_t Q_r/c)(c/q_t)^2(q^{*4}/S)$ for monatomic molecules	21
$J = J_\Phi (Q_t Q_r/c)(c/q_t q_r)^{1.2}(q^{*4}/S)$ for vapour consisting of linear polyatomic molecules	21
$J = J_\Phi (Q_t Q_r/c)(c/q_t q_r)(q^{*4}/S)$ for nonlinear molecules	21

*Symbols: ρ is the density of the liquid, r^* the radius of the critical nucleus, c the concentration of the molecules of the vapour, c_e the equilibrium concentration of the molecules of the vapour, a_c the accommodation coefficient, M the molecular weight, R the universal gas constant, N Avogadro's number, q_t and q_r the translational and rotational partition functions for the molecules of the vapour, Q_t and Q_r the corresponding partition functions for the critical aggregates, and d the diameter of the molecules of the vapour.

From the theory of the interphase boundary formulated by Gibbs, it follows logically that the surface tension should depend on the curvature of the surface of separation between the phases[23]. Kennan[24] put forward arguments justifying the monotonic decrease in σ with increase in the positive curvature of the surface. A quantitative expression for the relationship $\sigma = f(r)$, where r is the radius of the liquid drop, was first obtained by Tolman[25], who combined the basic equation of Gibbs' theory with the Gibbs–Kelvin equation relating the equilibrium pressure of the vapour above the drop and the curvature of the surface. By neglecting terms containing $1/r$ raised to powers > 1, Tolman obtained the following expression

$$\sigma/\sigma_0 = 1/[1+2(\delta/r)] \quad (9)$$

where δ is a quantity of the order of the interatomic distance, and σ_0 the tension of a flat surface.

Kirkwood and Buff[26] pointed out the inaccuracy in Tolman's arguments, due to the identification of the pressure

in a microscopic drop p' with the pressure in a macroscopic volume of liquid, and calculated the relationship $p'/(r)$ using Kirkwood's statistical theory, according to which the pressure in a liquid is determined by the intermolecular forces, described by the Lennard-Jones equation[27]. By taking account of only the interaction of pairs of nearest neighbours, Kirkwood and Buff obtained the same result as Tolman[25]. An even more rigorous derivation of Eqn. (9) was given by Hill[28]. As shown by Buff and Kirkwood[29], however, mere allowance for the relationship $\sigma(r)$ cannot improve the theory, since it is also necessary to make allowance for the change in the density of the drop with change in dimensions, due to the fact that the thickness of the Gibbs' interfacial layer becomes commensurate with the radius of the drop. Plesner[30] calculated the surface tension and radial density distribution in nuclei with dimensions 3–25 times greater than the dimensions of the molecule. To describe the behaviour in the drop, Plesner used Tonk's equation of state[31] for solid spheres with an attractive potential inversely proportional to the sixth power of the distance. Plesner's result is surprising—the surface tension of these droplets is independent of their dimensions and amounts to $\sim \sigma_0/3$. If we remember that the factor $\exp(-\Delta G^*/kT)$ close to critical supersaturation usually has a value $\sim e^{-50}$, we can see that a change in the surface tension by a factor of 3 corresponds to an increase in the rate of nucleus formation by a factor of $\sim 10^{15}$. Plesner's discovery that σ is independent of the curvature means that within a certain range of dimensions there should be a sharp decrease in σ with decrease in r. Since the relationship $\sigma(r)$ is not observed experimentally as far as values of the curvature equal to 10^6 cm^{-1}, this range must be fairly narrow. All this appears unlikely. An interesting feature is that, according to Plesner, very fine drops, even at their centres, do not have the same densities as macroscopic amounts of the liquid.

Shcherbakov[32,33] pointed out that the excess of free energy in very fine drops relates to the entire volume of the drop, and not merely to its surface. He also found that simple substitution of the relationship $\sigma(r)$ in Kelvin's equation cannot lead to the correct result, and that it is also necessary to introduce into this equation a term containing $d\sigma/dr$. This viewpoint was put forward by both Kelvin and Gibbs, but their opinion was based entirely on intuition. In Shcherbakov's theory, surface tension is regarded as a quantity equal to the excess free energy per unit surface area of the drop. The expression obtained by Shcherbakov for the quantity σ defined in this way has the form

$$\sigma = \sigma_0\left(1 - \frac{2}{kr} + \frac{2}{k^2r^2}\right) \qquad (10)$$

where $(1/k \simeq 0.2\text{–}0.5 \times 10^{-7}$ cm). Because of the third term, which increases with decrease in r, the function $\sigma(r)$ has a minimum, and at very small values of r it increases with decrease in the dimensions. This result does not agree with the results of published work[25–30] or with the conclusion recently reached by Bellemans[34] in a generalisation of the theory of the Mayer–Born–Fuchs equation of state[35] for the case of a system containing an interface of arbitrary curvature.

A monotonically decreasing relationship $\sigma(r)$ is also predicted by the theory of surface tension developed by Cahn and Hilliard[36,37] and Hart[38], based on the idea that the free energy density is a function of the concentration and concentration gradient of the molecules. The quantity ΔG in this theory can be calculated without introducing the surface tension, according to the formula

$$\Delta G = \int_V [f_0(c) + k(\nabla c)^2]\, dV \qquad (11)$$

where ∇c is the concentration gradient of the molecules, and $f_0(c)$ is the Helmholtz free energy for one molecule. On the spinodal, that is the line on the phase diagram whose equation, according to Gibbs, has the form

$$dP\,dV + dT\,dS + \Sigma\, dN\, d\mu = 0 \qquad (12)$$

ΔG becomes zero. As the spinodal is approached, according to this theory, the surface of the clusters becomes diffuse, and their radius tends to infinity. At low supersaturations, the Cahn–Hilliard–Hart theory predicts[38] a rate of nucleus formation close to that obtained from the classical theory. In recent years this theory has been further developed[39–42], and Hart[40] has reached an extremely important conclusion. In the Gibbs' theory of surface tension, the quantity σ is invariant with respect to the position of the interphase boundary in the intermediate range between the phases. For a curved surface, this invariance is not observed, and the calculated value of σ depends on the choice of position for the boundary between the phases. In this instance σ is found from the condition $d\sigma/dR = 0$, where R is the radial coordinate. Hart established that under certain conditions the function $\sigma(R)$ may not have a minimum, that is the free energy of the nucleus cannot always be separated into bulk and surface terms.

In the Cahn–Hilliard–Hart theory it is assumed that the changes in the concentration of the molecules are small at distances close to the value for the radius of action of the intermolecular forces. This assumption has been criticised by Hirth and Pound[43].

Reed[44] calculated the chemical potential of a molecular aggregate consisting of up to eight molecules by finding the sums with respect to states of the aggregates, regarding them as polyatomic molecules. He assumed that the interaction between nearest neighbours in the aggregate is described by the Lennard-Jones equation. Reed's theory is applicable to larger aggregates only with great difficulty, because of the increase in the magnitude of the calculations. In Reed's theory it is possible only to estimate the influence of the presence of isomeric configurations of the aggregates, consisting of the same number of molecules, on their equilibrium concentration. Kilpatrick and Katsura[45] developed a method for calculating the virial coefficients of vapours containing aggregates consisting of several (up to ten) molecules. This makes it possible to calculate the equilibrium values of the free energy of formation of these aggregates. Benson and Shuttleworth[46] calculated the free energy of a cluster containing 13 molecules, assuming that the molecules in the nucleus are close-packed, and making allowance only for the interaction of pairs of nearest neighbours.

In view of the successful development of work on the many-body problem[47], we can expect the development of a nucleus model in which the treatment is not restricted to the interaction of nearest neighbours.

In recent years, the problem of the contribution of the external degrees of freedom of the cluster to its free energy has been widely discussed. This problem was first examined by Frenkel'[48]. Having pointed out that the result obtained by the theory of nucleation without allowance for the contribution made by the rotational and translational movement of the cluster to the value of ΔG has no physical significance, Frenkel' assumed that in order to

take account of this contribution it is sufficient to exclude six internal degrees of freedom. For this purpose he replaced g by $g - 2$ in the expression for ΔG (7). The exclusion of six internal degrees of freedom in order to take account of the external degrees of freedom is quite logical, but for this purpose it would be sufficient to replace g by $g - 2$ only in the first term, that is the bulk term, in expression (7). Frenkel' did not introduce any arguments to explain why he carried out this substitution in both terms; this substitution produces almost no change in the value of ΔG, whereas replacement in only the bulk term would lead to an increase in the rate of nucleation by a factor of $\sim 10^{20}$.

Rodebush[17], in an examination of the problem of the absolute entropy of formation of clusters, also concluded that it is necessary to make allowance for the external degrees of freedom, but he subsequently concluded[40] that this contribution is taken into account automatically in the classical theory. Adams and Band[50] made allowance for the contribution of the translational degrees of freedom, neglecting rotational degrees of freedom. As pointed out by Kuhrt[18], with the introduction of a factor taking account of the external degrees of freedom into the statistical sum, it is necessary at the same time to exclude six vibrational degrees of freedom. The introduction of Kuhrt's correction for the example of the condensation of water vapour at supersaturations close to the critical supersaturation corresponds to an increase in the rate of nucleation by a factor of $\sim 10^8$.

Courtney[16] made allowance for the partial pressure of the clusters in the calculation of ΔG, and this led to an increase in the expression for J given by Frenkel'by a factor $1/S$, which may reach very large values at the concentration of the vapours of non-volatile substances. In his next paper[21], Courtney combined this result with Kuhrt's conclusions[18]. The expression which he obtained is given in the Table.

The problem of the absolute entropy of formation of nuclei was examined in detail by Lothe and Pound[19], Sundquist and Oriani[20], Hirth[51], Feder and coworkers[52], and Russell and coworkers[53]. The last of the works cited gives a logical summary of earlier work and formulates the following scheme, which makes it possible to find the free energy of formation of a cluster: n nuclei, containing g molecules, are formed from ng molecules of the vapour by five processes: 1) the vapour is compressed until saturated; 2) the vapour is condensed to liquid at constant temperature and pressure; 3) the liquid is supercooled to 0°K; 4) the liquid is divided reversibly into n portions; and 5) the clusters are heated to a temperature T.

By writing expressions for the changes in free energy corresponding to these processes, the authors cited[19,20,51-53] obtained an expression for the free energy of formation of a cluster. The equations which they obtained on this basis for the rate of nucleation are also given in the Table. These expressions give values for J which are greater by factors of 10^{17}–10^{18} than those obtained by Frenkel's solution. It should be noted, however, that despite the strictly logical nature of the arguments cited above, the numerical estimates of the influence of the contribution of the external degrees of freedom to the rate of nucleus formation, made in the works cited[19,20,51-53], are of doubtful accuracy. In the calculation of the term corresponding to the fifth stage in the above scheme, the authors cited mechanically applied the formulae for the translational and rotational components of the heat capacity of polyatomic molecules. A cluster, however, is a much looser formation than a polyatomic molecule, since the energy of the van der Waals' forces holding the molecules in the nucleus is much less than the energy of valency bonds. Thus, as pointed out by Vukolovich[54], the rotation of the cluster as a whole can be neglected. The theory developed by Vukolovich for the heat capacity of water vapour containing molecular associates, which ignores the external degrees of freedom of the associates, shows such good agreement with the experimental data that it has been possible on this basis to construct an accurate water vapour phase diagram, which has been widely used for several decades in technical calculations. Hirth and Pound's argument[10] that the rate of nucleus formation may be much less than the calculated value, since the probability of attachment of molecules may decrease considerably with increase in the curvature of the surface, reaching values as small as 10^{-17}, does not appear convincing. It is true, however, that Okuyama and Zung[55] predicted theoretically a decrease in the accommodation coefficient a_c for a drop radius $\leq 10^{-5}$ cm, but in their calculations they ignored the relationship $\sigma(r)$, which may weaken this effect considerably. It follows from the experimental data of Wakeshima and Takata[56] that a_c increases slightly with decrease in r.

Recently, the previously published conclusions[18,19,50-52] were convincingly criticised by Reiss and Katz[57], who showed that there is no justification for the assumption made by Lothe and Pound and subsequent workers that the expression (7) given for the value of the free energy of formation of a nucleus corresponds to an aggregate with a stationary centre of mass. After examining the classical theory in detail, Reiss and Katz concluded that it ignores only the contribution of the translational motion of the centre of mass. It is evident that this feature can be taken into account by introducing Courtney's correction $1/S$ into the expression for J. The other inaccuracy which they detected requires the introduction of a factor V_g/gV_1, where V_g is the volume of a cluster consisting of g molecules, and V_1 the volume of a single molecule. According to the estimates made by Reiss and Katz, this factor has values from 1 to 10.

Courtney[58] pointed out that even if the Lothe–Pound correction is correct, it does not mean an increase in the rate of nucleus formation by a factor as large as 10^{17}, since in this instance the greater part of the mass of the vapour should be present in aggregates with subcritical dimensions. The marked decrease in the concentration of single molecules of vapour resulting from this feature should be accompanied by a decrease in the equilibrium concentration of critical nuclei, and hence by a decrease in J.

In a number of recent papers, the determination of the rate of nucleus formation in first-order phase changes is examined on the basis of the general relationships of the thermodynamics of irreversible processes[52,59], but the conclusions reached in these papers are so general in character that it would be premature to discuss the results obtained in this direction.

The classical theory neglects the heating of the nuclei by the liberated heat of condensation. This is quite justified when the condensing vapour is a small impurity in a noncondensing gas, in which the collision of the molecules of the gas with the nuclei ensures dissipation of the heat of the phase change, but in practice we often have to deal with the condensation of vapour in the absence of a carrier gas, and the neglect of the heating effect becomes unjustified. Russell and Feder[52] solved the problem of nonisothermal formation of nuclei by examining the equation for the two-dimensional diffusion of clusters in the g–ϵ plane, where ϵ

is the thermal energy of the cluster. Similar work was carried out by Bakhanov and Buikov[60].

All the expressions given in the Table describe nucleus formation under steady-state conditions. In a non-steady-state process, however, J is a function of time t. The problem of nucleus formation in non-steady-state conditions, arising in the instantaneous production of supersaturation, has been examined by a number of authors, including Zel'dovich[5], Collins[61], Wakeshima[62,63], Kantrowitz[64], and Frisch[65], who solved a time-dependent equation of form (3), with the assumption that at the initial moment of time the vapour is completely monomolecular and that the diffusion coefficient along the g axis:

$$D = (36\pi)^{1/3} v g^{2/3} p / \sqrt{2\pi m k T} \qquad (13)$$

is independent of g. Here, v is the volume occupied by one molecule in the liquid. The result obtained by these authors can be written in the form

$$J = J_0 \exp(-k^2/zt) \qquad (14)$$

where z is the rate of growth of the particles in molecules per second, and k a constant whose order of magnitude is equal to that of the number of molecules in the nucleus. The specific values obtained by different authors[5,61-64] for the time interval $\tau_{0.9}$ after which J reaches values equal to 0.9 times its steady-state value, differ considerably; the values lie in the range 10^{-5}–10^{-6} s, and $\tau_{0.9}$ increases with decrease in the probability of attachment. Wakeshima[62] and Frisch[65] tried to make allowance for the influence of associates in the vapour on the rate of attainment of the steady-state. Wakeshima found that in this instance the rate of attainment of the steady state is increased, but Frisch reached the opposite conclusion. It should be noted that there is an error, pointed out by Courtney[66], in Frisch's mathematical calculations.

To estimate the time required for steady-state conditions to be established, it is necessary to alter the relationship $J(t)$. It is possible to determine the time interval after which the concentration of critical nuclei reaches, let us say, 50% of its steady-state value. Andres and Boudart[67] solved Eqn. (3) by the method of statistical moments. The values which they obtained for $\tau_{0.5}$ are smaller by an order of magnitude than the values of $\tau_{0.9}$ obtained by other workers[3,62-65]. A simple approximate expression for $\tau_{0.9}$ was obtained by Farley[68]:

$$\tau_{0.9} = 25 g^{*2} \sqrt{2\pi m k T} / 4\pi r^{*2} \rho$$

A third method for studying the problem of the attainment of the steady state involves numerical solution of a system of equations of type (1) for all values of g from 1 to a certain value of $g > g^*$. The first attempts of this kind were made by Christiansen[69] and Turnbull[70], who solved systems of 4 and 25 equations respectively. Courtney[71] used a computer to solve a system of equations describing the changes with time in the concentrations of clusters containing from 20 to 120 molecules. The calculations were carried out for the condensation of water vapour at −10°, −40°, and −60°C and supersaturations of 5.0 and 6.0. Courtney assumed that for nuclei with $g < 20$ the equilibrium concentration is reached instantaneously. Under these conditions, $\tau_{0.95}$ amounted to 1.5–27 μs. This is smaller by a factor of about 2–3 than that obtained from the published relationships[62-65] and is fairly close to the values which can be obtained using Farley's formula[68]. For values of $S = 5$, Courtney obtained values of $\tau_{0.95}$ which were smaller by a factor of ~ 10 than those obtained for $S = 6$. The calculations were carried out with the assumption that $a_c = 1$.

Chakraverty[72] recently solved Eqn. (3) without making any assumptions regarding the quantities α_g and β_g, which were regarded as unknown functions of g. His results show qualitative agreement with Courtney's conclusions[71] and order of magnitude agreement is also observed in the values of τ.

As pointed out by Sutugin and Fuchs[73], steady-state conditions are not attained in practice at very high supersaturations, since the supersaturation changes considerably throughout the entire process of nucleation, whose duration may not exceed 10^{-5} s. Under these conditions, calculation of nucleus formation is possible only by solving a system of equations of type (1). The problem is then simplified, since under conditions of high supersaturation the dimensions of the critical nucleus are very small and the number of equations in the system is also small. Moreover, the total duration of the process becomes commensurate with the time interval within which the nucleus collides with an average of one molecule of the vapour. This makes possible a simple calculation of the quantity of vapour involved in molecular collisions with nuclei with all dimensions represented, and also with the growing supercritical particles, and this makes it possible to avoid the assumption, which is usually made in the classical theory, that the supercritical particles are removed from the system and replaced by an equal mass of vapour.

An attempt to make allowance for the influence of the heat of condensation during the attainment of the steady state was made by Probstein[74], who expressed the probability of volatilisation of a molecule from the growing nucleus as follows:

$$\beta_g' = \beta_g \left[1 + \theta \frac{U_\infty}{RT^2} \right] \qquad (15)$$

where β_g is the probability of volatilisation under isothermal conditions, U_∞ the heat of condensation, $\theta = J_g U_\infty c m / f_g F \alpha_g a_c l$, f_g the distribution function for the concentrations of the clusters, and l the heat capacity. Probstein introduced a new time $t' = t/[1 + U_\infty^2 c_1 m / l a_c R T^2]$ and solved Eqn. (3). The method of solution which he used is analogous to the method of Kantrowitz, but since allowance was made for the heat of condensation it was found that the attainment of the steady state requires a time interval which is several times larger. As pointed out by Feder and Russell[52], a fundamental study of the problem of non-steady-state nucleus formation under nonisothermal conditions requires the solution of a three-dimensional diffusion equation in g–ϵ–t space, and this presents insurmountable difficulties. The approximate estimates which they made showed that the liberation of the heat of condensation during the formation of nuclei in water vapour under the conditions which usually exist in experiments with a Wilson chamber may lead to an increase in $\tau_{0.9}$ by a factor of 2–3 compared with isothermal conditions.

Luke[75] solved the problem of the rate of cooling of hot atoms of a metal suddenly placed in a cold inert gas. When the concentration of metal vapour is low, the excess of thermal energy of the atom is reduced by a factor of 2 in a time interval of ~ 10^{-7} s. From this it may be concluded that if the mass of condensing vapour amounts to only a small fraction of the total mass of the vapour–gas mixture, the liberation of the latent heat of the phase change may not have a marked influence on the value of J.

On going to the problem of limiting supersaturation, it is necessary first of all to note that there are at least two interpretations of this concept. The first interpretation is related to the fact that the dimensions of the cluster

cannot be less than the distance between the centres of the molecules in the liquid (or the solid). This was first pointed out by Frenkel'[7], whose viewpoint was supported by other workers[76-78] who tried to calculate the maximal supersaturation using the Gibbs–Kelvin equation, which obviously cannot be used for this purpose. Bykov and Teverovskii[76] assumed that the weak dependence of the rate of nucleation in water vapour on its supersaturation, observed by a number of workers, can be attributed to the attainment of limiting supersaturation. In Bykov and Teverovskii's own experiments, however, only the magnitude of the critical nucleus calculated according to the Gibbs–Kelvin equation remained constant, and the rate of formation of the nuclei changed considerably with change in the supersaturation.

The second concept of limiting supersaturation is based on the idea that under certain conditions the work of formation of the nucleus should become zero. The theory of second-order capillary effects, developed by Shcherbakov[79] and the Cahn–Hilliard–Hart theory[35-37], in particular, lead to this conclusion. From this concept it follows that the nucleus corresponding to limiting supersaturation may contain tens or hundreds of molecules. The formula put forward by Shcherbakov and coworkers[32,79] for calculating the limiting supersaturation contains the macroscopic density of the liquid. It follows from published work[35-38], however, that as the spinodal is approached the density of the nuclei decreases, approaching the density of the vapour.

A number of authors[80-82] consider that ΔG^* does not become equal to zero even on the spinodal. This view is contrary to Gibbs' classical theory of surface tension. Gibbs[12] in fact showed that the work of formation of a nucleus amounts to $\frac{1}{3}\sigma F$, where F is the surface area of the nucleus. Rusanov[83] pointed out that if σ becomes zero, ΔG should also become zero. Thus this concept should be correct at least for the condensation of vapour close to the critical point.

The conclusion that the minimal nucleus should contain much more than two molecules, that is that there is no vapour pressure with which very small aggregates can be in equilibrium, follows from the work of Shcherbakov[32,33], Bakhanov and Buikov[84], and Cahn, Hilliard, and Hart[35-37]. This conclusion is not completely general, however, since calculations[16,73] have shown that in the supersaturated rarefied vapours of substances with low volatility the minimum of the $\Delta G(g)$ relationship may correspond to dimers or even monomeric molecules. For the condensation of the vapours of these substances with low volatility, the concept of limiting supersaturation can be derived from the following considerations. Let us assume that we have a mixture of the vapour and a noncondensing gas. Let us cool this mixture along the isochore to a temperature at which the critical nucleus contains two molecules. The concentration of the dimer (with the condition that constant supersaturation is maintained) will be determined by the ratio of the rates of formation and breakdown of the dimeric molecules. With decrease in temperature the rate of the first process will decrease comparatively slowly, since the number of collisions between the molecules is proportional to $T^{1/2}$, whereas the second process stops almost completely at a certain temperature (this follows from calculations for rarefied silver vapour[73]). Thus the rate of formation of the critical nuclei—dimers—will first increase due to the decrease in the rate of breakdown, and then decrease as a result of the decreased number of collisions between individual molecules. Limiting supersaturation, at which the rate of nucleus formation is determined exclusively by the frequency of the collisions between individual molecules, can be obtained only in the condensation of a vapour with a sufficiently low partial pressure, otherwise exhaustion of the vapour phase takes place during the cooling of the vapour–gas mixture.

In Kachurin's opinion[85], at high supersaturations the rate of nucleus formation should be appreciably greater than that obtained in the classical theory, since in this instance, in addition to the gradual increase in heterophase fluctuations, we may have conversion of homophase fluctuations (that is fluctuations not exhibiting the structure of the new phase) into heterophase fluctuations. On the other hand, it follows from the Cahn–Hilliard–Hart theory[36-38] that as the spinodal is approached the difference between homophase and heterophase fluctuations should disappear.

As already noted, the classical theory considers only the condensation of a one-component monomolecular vapour. The vapours of most substances, however, consist of mixtures of associates. A generalised equation taking account of the possibility of collision with one another for associates and subcritical nuclei of different dimensions can be written in the form

$$\frac{dW_g}{dt} = -\sum_{j=0}^{N+1} K_{jg}W_g + \sum_{j=0}^{N} K_{gj}W_j, \quad g, j = 1, 2 \ldots N$$

where Kjg is the probability of conversion of nucleus j into g, and Kgj the probability of the reverse change. The analytical solution of this equation presents considerable difficulty. Frisch and Willis[86] carried out the analytical solution of a simplified equation describing nucleus formation in a vapour consisting of a mixture of the dimer and monomer. Courtney[21] used numerical methods for the same purpose. According to his results, nucleus formation should take place several times more rapidly in the presence of dimers. As correctly pointed out by Katz and Salsburg[87], however, the authors cited[21,86] neglected the decrease in supersaturation due to the fact that part of the mass of the vapour is included in the dimer. In fact, the equilibrium concentration of critical nuclei is proportional to the concentration of monomolecular vapour [(Eqn. (2)], so that association should decrease the rate of nucleus formation. An analogous conclusion was reached by Sutugin and Fuchs[73], who calculated the condensation of silver vapour for the conditions where an appreciable proportion of the condensing substance is included in subcritical associates.

Nucleus formation in a two-component condensing vapour has been examined theoretically by Neumann and Doring[88] and also by Reiss[89].

In addition to the above theory, based on the Szilard–Farkas model, attempts have been made to develop other theories of phase transformations. Expressions for the equilibrium concentrations of nuclei are obtained in the Mayer–Born–Fuchs equation of state theory[38]. The general form of these expressions is similar to that of Frenkel''s equation for the equilibrium concentration of a nucleus with given dimensions, but the determination of the equilibrium concentrations in the Mayer–Born–Fuchs theory requires extremely tedious calculation of the so-called group integrals, which take account of the contribution of the interaction between pairs of molecules making up the cluster to the statistical sum for the cluster. The problem is complicated considerably by the need to calculate the group integrals for all possible isomeric configurations. Recently, however, considerable progress has been made in this direction. Kilpatrick and Katsura[45] and Barker and Leonard[90] developed a relatively simple method for calculating the group integrals for nuclei

containing up to ten molecules. These authors were able to calculate even the fifth virial coefficient of a gas containing associates. Since during condensation the concentrations of small ($g < 10$) nuclei are almost the same as the equilibrium concentrations, the latest results of the theory of the equation of state may be useful for calculations of nucleus formation at high supersaturations.

In the opinion of Christiansen[91] and La Mer[92], the nucleus of liquid phase in a vapour should contain not more than 4–5 molecules, which is considerably less than the number assumed in the classical theory. They also assumed that for each substance the dimensions of the nucleus should depend very little on temperature, the concentration of the molecules of the vapour, and the supersaturation. Courtney[93] described this model as the "constant-number theory" and pointed out that it should be suitable for the description of nucleus formation in substances with a high intermolecular interaction potential. Sutugin and Fuchs[73] calculated nucleus formation in silver vapour condensing as a result of the cooling in a submerged stream at concentrations of 10^{16}, 10^{15}, and 10^{14} molecules cm^{-3}, and found that the dimensions of the nucleus should correspond to 5–6 molecules for the first two concentrations. For the third concentration, the rate of nucleation became appreciable when the nucleus contained six atoms, after which the cross-section of the nucleus decreased with increase in supersaturation, and for the greater part of the total duration of the process the nucleus consisted of only two atoms. For all three concentrations, the supersaturation increased by several orders of magnitude during nucleus formation. From this it follows that at high supersaturation the dimensions of the nucleus in fact change little.

Independent attempts to develop a theory of nucleus formation which does not make use of the Szilard–Farkas model have been made by Reiss[94] and Hill[95], but the models which they have proposed have been insufficiently developed, and it would be premature to discuss their importance.

Results useful for an understanding of the initial stage of the formation of associates were obtained by Storgyn and Hirshfelder[96], who examined the problem of the lifetime of a combination of two molecules, formed by the collision of two single molecules, or, in other words, the problem of the duration of collisions in pairs. These authors calculated the duration of the collisions of pairs in inert gases, with the assumption that the interaction between the molecules is described by the Lennard-Jones equation. The method which they developed makes it possible to calculate both the kinetics of formation of the dimers and their equilibrium concentration, but only by using computers.

Vukolovich's equation of state theory[54] was used by Nikandrov[97,98] to calculate the concentration of aggregates in water vapour for $S = 1$.

All that has been said in this section refers to the formation of the nuclei of a liquid phase in vapours, but since experimental data indicate that the particles of condensation aerosols are amorphous, particularly when the condensation takes place at high supersaturations[99–103], it may be assumed that in most instances the condensation of a vapour in bulk leads to the formation of nuclei of a liquid phase, which can crystallise only subsequently. According to data obtained by different authors, the condensation of water vapour below −40°C or below −65°C leads to the formation of ice nuclei, but this has been disputed by Dufour and Defay[104], who considered that ice is formed only by the freezing of water droplets produced from the vapour.

Unlike the nuclei of the liquid phase, crystalline nuclei are characterised by anisotropy of the surface energy. Because of the small dimensions of the nuclei, a marked contribution to the surface energy is made by the apices, edges, steps, and fractures on the surface of the faces. The growth of droplet nuclei includes only one process—the adsorption of molecules from the vapour phase—whereas the formation of a crystallite should include four molecular processes: the adsorption of molecules of the vapour on the surface, the nucleation of two-dimensional discs on the surface of the faces, surface diffusion, and the attachment of molecules to elementary steps, the free energy of formation of the crystallite being a monotonic function of the number of molecules of which it is made up. Stranski and Kaischev[105,106] and Carrera and Burton[107] examined the process of crystal formation, taking account of only the formation of two-dimensional discs on the faces, and assuming that in nucleation the concentrations of the clusters are equal to the equilibrium concentrations. An expression for the rate of formation of crystalline nuclei, including a non-equilibrium factor, was obtained by Becker and Doring[3,108], who calculated the bond energy of the nucleus using a model involving the interaction between pairs of nearest neighbours. Taylor[109] solved the problem of the bond energy for the crystalline nuclei of alkali metal halides, containing up to 13 molecules, by means of the quantum theory of first-order perturbations. When calculating the free energy of crystalline nuclei, as for the nuclei of a liquid phase, it is necessary to take account of the contribution made by the external degrees of freedom.

III. METHODS OF CALCULATING THE FORMATION OF CONDENSATION AEROSOLS

In the formation of a condensation aerosol, the formation and condensation growth of nuclei take place simultaneously. The consumption of vapour for the growth of the particles leads to a decrease in the supersaturation, and nucleation stops. Thus the calculation of the number and dimensions of the particles formed should make allowance for both these processes, and also for coagulation at high concentrations of the particles formed.

Calculation methods of this kind are required for comparing theory with experiment, and also for predicting the parameters of aerosols formed in various technological processes.

Existing methods of calculation can be divided into analytical and computational. The analytical method for calculating the formation of an aerosol during the adiabatic expansion of a gas containing the vapour of a condensable substance was first developed by Tunitskii[110], who carried out the simultaneous solution of the equations for conservation of mass of the condensing substance and for rate of formation of nuclei, assuming the temperature to be constant. He obtained two expressions for the number of drops formed. In the derivation of one of these expressions it was assumed that the rate of growth of the drops is determined by a gas-kinetic mechanism, and in the second instance a diffusion mechanism was assumed. Tunitskii also estimated the error introduced by neglecting the heat of condensation.

Oswatitsch[111,112] developed an analytical method for calculating the change in the number of drops and the mass of condensate during the condensation of vapour in a Laval nozzle. For this purpose he carried out the simultaneous solution of four differential equations: the continuity equation and the equations for the preservation of momentum,

preservation of energy, and condensation. The problem of aerosol formation during the adiabatic cooling of a vapour–gas mixture was also solved by Corner[113], and later by Bakhanov and Buikov[60], who took account of heat exchange with the external medium and the change in temperature resulting from the heat of condensation. Any of the steady-state solutions for the rate of nucleus formation can be used in any of the above methods of calculation.

Raizer[114] solved the problem of condensation in a cloud of vapour undergoing adiabatic expansion into a vacuum, but he neglected the liberation of the heat of condensation, and this is inadmissible in the examination of condensation in the absence of a noncondensing gas capable of dissipating the energy of the phase change.

Disadvantages common to all analytical methods of calculation include the need for simplifying assumptions in the derivation, and also the fact that these methods can predict only the number of particles formed and their mean dimensions, and not the parameters of the size distribution. Analytical methods of calculation cannot include an examination of coagulation. In the calculation of the growth of the particles it is necessary to assume that throughout the entire process, growth takes place by a single mechanism, whereas the mechanism changes with increase in the dimensions of the particles. An analytical solution is also impossible if the temperature and concentration are functions of more than one variable[115–117]. Because of these features, methods for the successive calculation of the condensation, in which the duration of the process is broken down into tens or hundreds of intervals or stages, have been widely used. It is assumed that in each range of temperature, the concentration and other significant parameters remain constant, and that they undergo sudden changes on going to the next interval. The number of nuclei formed in each interval, and the growth of the particles previously formed, are calculated.

Amelin[118] described a program for calculating the condensation when a turbulent vapour–gas stream is cooled in a heat exchanger, Griffin and Sherman[119], Stever[120], and Hill, Wittig, and Demetri[121] described in detail stepwise methods for calculating the condensation in Laval nozzles, and Lund and Rivers[122] described methods for calculating the condensation in a Wilson chamber.

In the works cited, the calculations were carried out for situations where the supersaturation depends only on time or only on the coordinate. Higuchi and O'Konski[123] put forward a method for determining the number of nuclei formed in the zone in which a hot inner stream mixed with a cold surrounding gas. They expressed the number of particles formed in unit time by means of the integral $\int_0^\infty J(n)\frac{dV(n)}{dn}dn$, where $V(n)$ is the volume of the mixing zone bounded by a surface with constant value n, that is the ratio, averaged with respect to time, of the weight concentrations of the cold and hot gases. Higuchi and O'Konski neglected the quantity of vapour used up in the growth of the particles, and assumed that the supersaturation falls below the critical value entirely as a result of the dilution of the condensing mixture by fresh portions of cold gas. This is quite justifiable, if the supersaturation exceeds the critical value only in a very small part of the mixing zone of the stream S. If however high supersaturations are reached in the zone in which the hot vapour–gas stream mixes with cold air, the quantity of vapour used up cannot be neglected. Sutugin and Fuchs[73] developed a method for the stepwise calculation of the condensation in the stream, in which the entire mixing zone is broken down into intervals whose boundaries are the n-const surfaces. A program for calculating the formation of an aerosol under conditions in which fresh portions of condensing gas are formed continuously as a result of a chemical reaction in the gaseous phase was compiled by Dunham[124].

Carstens and coworkers[125] carried out a numerical estimation of the decrease in the rate of nucleus formation due to the decrease in the concentration of vapour close to the growing particles, and found that this effect is extremely small.

Friedlander[126] put forward a calculation of the formation of condensation aerosols in a submerged stream by means of the theory of similarity and calculated the dimensionless criteria, whose function should be the dimensions of the particles of the resulting aerosol. Like all methods based on the use of the theory of similarity, Friedlander's method requires the preliminary empirical determination of the dependence of the parameters sought on each of the criteria, the number of which may vary from 4 to 8. It is therefore not surprising that this method has not yet found application.

The formation of aerosols at high supersaturations is often accompanied by coagulation, and, as pointed out by Petryanov and Tunitskii[127], it is coagulation which should determine the degree of dispersion of the aerosols formed under these conditions. As a rule, polydisperse aerosols are formed during spontaneous condensation. A number of recent papers[128–130] are devoted to numerical methods for calculating the coagulation of aerosols by integration of a system of equations of the form:

$$\frac{dn_i}{dt} = \sum_{j+k=i} K_{jk}n_jn_k - \sum_{l=1}^{\infty} K_{jl}n_jn_l$$

where n_i is the concentration of particles formed from i primary particles, and K_{jk} the collisional rate coefficients. The volume of the calculations increases with increase in the degree of coagulation, so that this method cannot be used to calculate the coagulation leading to an increase in the dimensions of the particles by a factor of more than ~ 100. Rosinski and Snow[131] proposed a simplified scheme for the calculation of coagulation. According to the ideas of these authors, the continuous distribution function of the aerosol particles with respect to dimensions is replaced by a discontinuous function, and it is assumed that the aerosol consists entirely of particles in which the numbers of molecules are given by the figures 2^i, where i is an integer. The collisions of particles of the 2^i classes leads to the formation of particles of the 2^{i+1} class. It is then arbitrarily assumed that the collisions of particles of classes 2^i and 2^{i-1} also leads to the formation of particles of class 2^{i+1}, but in an amount corresponding to $(2^i + 2^{i-1})/2^{i+1}$ times the number of particles of class 2^i taking part in the collisions. In the collisions of particles of classes 2^i and 2^{i-j}, where $j > 1$, however, the dimensions of the former remains unchanged, but their number increases by a factor of $(2^i + 2^{i-j})/2^i$. This scheme was used by Stockham[132] for calculations on silver vapour, and he assumed that the collision of two atoms leads irreversibly to the formation of a twin, etc. As shown by Sutugin and Fuchs[73], this is justifiable only at sufficiently low concentrations of vapour and a high rate of cooling of the vapour–gas mixture, but since the size distribution of the aerosol finally obtained is still determined by the coagulation, Stockham's results are of undoubted value. He found that Rosinski and Snow's scheme correctly predicts the degree of dispersion of the resulting aerosols if values approximately twice those obtained in the formula for the number of collisions between gas molecules are used for the coagulation constant in the

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calculations. This last feature confirms Fuchs and Sutugin's theoretical and experimental conclusions[133] that the forces of intermolecular interaction should increase considerably the coagulation constant of highly dispersed aerosols. In later work[73], the value 2.21 was obtained for the factor corresponding to the increase in the rate of coagulation of silver particles as a result of molecular forces.

Strictly speaking, the forces of intermolecular interaction should also influence the condensation growth of highly dispersed aerosols, but the introduction of a correction analogous to Sutherland's correction can hardly be meaningful, since there are almost no data on the magnitude of the condensation coefficient and its dependence on the curvature of the surface on which the condensation is taking place.

IV. EXPERIMENTAL STUDIES OF THE FORMATION OF CONDENSATION AEROSOLS

The aim of the experimental study of this phenomenon may be the determination of the critical supersaturation for a given substance and the temperature dependence of the critical supersaturation, or the determination of the dependence of the rate of nucleation on supersaturation and the influence of various factors on this rate. The development of the size distribution of particles during the formation of a condensation aerosol is of considerable interest.

The chief difference between existing methods for studying spontaneous condensation lies in the methods for the production of the supersaturation in the condensing vapour; this may be brought about by adiabatic cooling of the vapour or vapour–gas mixture (Wilson cloud chamber and Laval nozzle), by heat exchange through the walls of the apparatus, and by mixing gas streams at different temperatures.

The oldest instrument used to study spontaneous condensation is the Wilson cloud chamber[134]. Adiabatic expansion in a Wilson chamber can be brought about by means of a piston, a diaphragm, or a bellows, or by suddenly connecting the working volume to a vacuum reservoir. A number of workers have studied the problem of the adiabatic nature of the expansion taking place in the chamber. Flood[135] concluded that the expansion is adiabatic so long as the volume of the chamber is not less than 1 litre, and the degree of expansion not less than 1.4, but Stachorska[136], using an inertia-free temperature recorder, proved that the expansion is non-adiabatic in a chamber with a volume of 1 litre even for expansions of 1.2, and concluded that it is necessary to use a chamber with a volume of 30 litre, in which Thomson's equation for the adiabatic decrease in temperature is obeyed rigorously. The use of a large chamber is also desirable in order to decrease the loss of vapour and nuclei as a result of diffusional deposition on the walls.

These features restrict the application of the Wilson chamber to the range of low supersaturations. Since at supersaturations which are not too much greater than the critical supersaturation the number of nuclei formed is limited, it is necessary to take careful precautions to remove foreign condensation nuclei (including ions) from the chamber. For this purpose the chamber is filled with a filtered gas; before the start of the main measurements, several successive expansions are carried out, and the foreign condensation nuclei become larger as a result of the condensation of vapour, and are deposited on the floor of the chamber. Ions are removed by applying an electrical field.

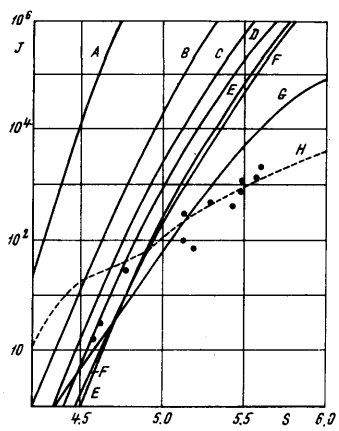
Since the end of last century, the Wilson chamber has been used many times to determine the critical supersaturation in the vapours of water, alcohols, and various other liquids, and the data obtained by its use over several decades were assumed to provide irrefutable proof of the correctness of the classical theory. Recently, however, a different viewpoint has been put forward[137-139]. Mason[137], in an examination of data on critical supersaturation obtained by Wilson and Powell[140], Volmer and Flood[141], Frey[142], Sander and Dahmkohler[143], Barnard[144], and Pound and coworkers[138], pointed out that Wilson and Powell[140] used an unsatisfactory method for detecting the start of condensation, and that the other authors cited[141-143] took inadequate measures to eliminate foreign condensation nuclei. In the much more thorough work of Barnard[144], Pound and coworkers[138], and Madonna and coworkers[139], the experimental values of the critical supersaturation coincided with the theoretical values only at temperatures $< 260°C$. Pound and coworkers[138] and Madonna and coworkers[139], like Mason[137], consider that in all work on the study of spontaneous condensation in the Wilson chamber, condensation on ions or foreign particles was in fact observed. Hollomon and Turnbull[145] found that the Volmer–Flood formula effectively predicts the critical supersaturation in the vapours of water and a number of organic liquids. Clark and Rodebush[146] found that different values are obtained for the critical supersaturation in water vapour when He or N_2 are used as inert gas. Madonna and coworkers[139] observed the same effect for the condensation of water vapour in O_2 and N_2, but Courtney[147] did not observe this effect. The scatter in the experimental values of the critical supersaturation in Courtney's work, however, was very high, even in the same carrier gas.

A number of papers have been devoted to a comparison of experimental data on the rate of nucleation with steady-state solutions of the classical theory. The rate of nucleation can be measured if the concentration of particles formed and the time interval during which they are formed are known. The first work in this direction[141,142,148,149] suffered from a large number of unsatisfactory experimental features, and the response time of the chambers in these experiments was not determined, so that it is not surprising that their results showed poor agreement with Tunitskii's calculations[110].

Stachorska[150], in a study of the condensation of C_2H_5OH vapour, obtained very good agreement with the results of his own calculations, based on Frenkel''s equation with allowance for the quantity of vapour used up in the growth of the particles. The results of Allard and Kassner[151], Kassner and Schmidt[152], and Schuster and Good[153] show good agreement with the calculations of Courtney[71] and of Lund and Rivers[154]. Although Courtney's calculations[71] were carried out using the Frenkel'–Courtney equation (see Table), whereas Lund and Rivers[154] used the Becker–Doring equation, these two equations differ only in a small numerical factor. At low supersaturations, both equations are readily justified within the limits of experimental error, but at high supersaturations the Frenkel'–Courtney equation is better. The introduction of the Courtney correction $1/S$ would also improve the agreement with theory in Stachorska's experiments, particularly at higher supersaturations, where this correction is greater. The results of the comparison of theory and experiment are given in Fig. 1.

Edwards and Woodbury[155] studied nucleus formation in supersaturated ^4He vapour. Since their experiments were carried out at absolute temperatures of several degrees,

it may be assumed that heterogeneous formation of nuclei did not take place, since at such low temperatures, no substance is capable of generating condensation nuclei. Edwards and Woodbury found that the rate of nucleation is greater by several orders of magnitude than that predicted by the classical theory, and depends to a marked extent on the supersaturation. The number of particles formed in these experiments was very large, and this made it impossible to attribute the results to condensation on ions which might have remained in the chamber after the application of the electric field. This discrepancy is possibly due to anomalous physical properties in liquid helium.



Theoretical and experimental data on the dependence of the rate of nucleus formation in cm^{-3} s^{-1} on the supersaturation for water vapour in an atmosphere of helium at −5°C from various papers. Theoretical curves: A,[143] B,[1] C,[4] D,[68] E,[3] F,[2] and G,[66]. Experimental data: H[152] and solid circles[151].

In the calculation of the rate of nucleation in the works cited, the values of the surface tension for a flat liquid surface were assumed. Pound and La Mer[156] and Byers and Chary[157] compared experimental results with the calculation of $J(S)$ with allowance for the relationship $\sigma(r)$ found by Tolman, and found that the agreement between theory and experiment is lower when allowance is made for this relationship.

Nucleation under non-steady-state conditions was studied by Allard and Kassner[151] using a Wilson chamber with two-stage expansion. The second, slow stage of the expansion was carried out in order to compensate for the increase in temperature resulting from heat exchange. This precaution was necessary, since the duration of the condensation in their experiments was greater than usual. The number of drops formed was recorded by fast cinematography. According to Allard and Kassner[151], the rate of increase in J shows satisfactory agreement with Courtney's calculations[71], but as the vapour is exhausted the rate of decrease in J is less than that given by the calculations. A number of papers[138,139,143] describe the study of the formation of ice crystals in supersaturated water vapour at low temperatures. The formation of the ice crystals was detected from the freezing of supercooled sugar solution placed in the Wilson chamber. The freezing of the solution is initiated by ice crystals deposited from the chamber. Although in the works cited the formation of ice crystals was detected at temperatures below the range between −40° and −65°C, Mason and Maybank[158] and Mason[137] point out that there is no proof that the crystals were formed from the vapour, and not by the crystallisation of nuclei of supercooled liquid. Changes in the mechanism of the formation of nuclei could not be detected[139] in butanol vapour at temperatures as low as −75°C.

Flood[159] studied nucleation in a binary mixture of water and C_2H_5OH vapours and obtained good agreement with the theory of Neumann and Doring[68], but Flood's experiments[159] suffered from all the unsatisfactory features characteristic of early work with the Wilson chamber, so that it must be accepted that further study of nucleus formation in binary mixtures is required.

In concluding the examination of results obtained using the Wilson chamber, it may be noted that work carried out in recent years provides quantitative confirmation of the correctness of the classical theory, and of all the equations, Frenkel's equation with Courtney's correction is satisfied with greatest accuracy.

Recently, the study of condensation in supersonic aerodynamic nozzles has acquired considerable importance. Here, as in the Wilson chamber, supersaturation is established by adiabatic cooling. For all substances except helium, the decrease in the equilibrium vapour pressure due to the decrease in temperature on adiabatic cooling takes place more rapidly than the decrease in the static pressure, so that sufficiently great isoentropic expansion of the vapour–gas mixture or even the pure gas may lead to the production of high supersaturations. If the flow of the stream in a Laval nozzle is not accompanied by condensation, the change in the static pressure (that is the pressure which can be measured by an instrument moving with the stream) is described by the equation for an adiabatic process. The condensation of vapour leads to a sudden increase in pressure, proportional to the mass of the condensed substance, relative to the "dry" isoentropy, and an increase in temperature as a result of the liberation of the heat of condensation. Experimental methods for studying condensation in Laval nozzles are based on measurement of the distribution of the static pressure and temperature along the axis and comparison of the results obtained with the "dry" isoentropy. The magnitude of the deviation of the pressure from the dry isoentropy can be calculated by one of the methods mentioned in section III, and the comparison of the calculated and experimental values forms the basis of methods for verifying theories of condensation. Thus comparison of theory and experiment in this instance is carried out indirectly. Detection of fog formation by optical methods is also used, but since the droplets begin to produce appreciable light scattering only when they reach dimensions of 10^{-6} cm, the formation of the fog is detected with a slight delay, which may amount to 10^{-4} s. This last feature, which is not taken into account, has in turn been responsible for the erroneous opinion that a long time interval is required for the attainment of the steady state in nucleation[160].

Oswatitsch[111] showed that the experimental data of Binnie and Woods[161] and Yellot[162] on the condensation of water vapour can be correctly approximated by the results of theoretical calculations with appropriate selection of the values for the surface tension of water. Gyarmathy and Meyer[163] obtained quantitative agreement between their own analytical calculations based on Frenkel's equation

and experiments on the condensation of sodium and water vapours. Wegener and Pouring[164] established that the results of the study of the condensation of water vapour can be approximated by any of the equations of Frenkel', Yang, Becker and Doring, or Barnard, with the selection of appropriate values for the accommodation coefficient.

A number of papers have described the study of the condensation of nitrogen in Laval nozzles. Comparison of the results of this work with calculations is made difficult by the absence in this instance of a noncondensing gas, so that the heating of the growing particles by the heat of condensation cannot be neglected. Moreover, in the presence of various impurities, such as CO_2 and H_2O, heterogeneous condensation in fact take place[165,166], since the impurities, which condense before the start of the condensation of nitrogen, form condensation nuclei. Thus only the experiments on the condensation of pure dry nitrogen are of interest. Studies of this kind carried out by various authors have given results which show good agreement with one another[167,168]. Some of these data were compared by Griffin and Sherman[169] with the results of a stepwise calculation of condensation using Courtney's equation[16] and were found to show good agreement with these calculations. Quantitative comparison of theoretical calculations with the results of experiments in Laval nozzles leads to the conclusion that the discrepancy does not exceed the error in the calculations and the error in the measurements, which are fairly high. Qualitative agreement between experimental and calculated data was obtained by Norgen[170,171] who collected particles of aluminium and mercury chlorides formed by condensation of the corresponding vapours in a laval nozzle and studied them on an electron microscope. Thomann[172,173] found that crystals of ice with dimensions ~ 14 Å are formed by condensation of water vapour in a supersonic jet.

In addition to condensation in aerodynamic tubes, which have been studied by a number of workers[161-173], condensation in gas streams flowing through a nozzle with small diameter into a high vacuum has been studied intensively in recent years. By using a nozzle cooled with liquid helium it is possible to obtain streams with Mach numbers of up to 100 and a temperature of the order of several degrees Kelvin. An apparatus of this kind has been described in detail by Kantrowitz and Grey[174], and by Becker, Klingerhofer, and Lohse[175]. The flow of H_2, N_2, and He at a pressure of ~ 600 mmHg into a vacuum of ~ 10^{-5} mmHg has been studied[175]. The density of the flowing beams was varied in the range 10^{15}–10^{19} molecules cm^{-2} s^{-1}. It was established that the addition of another gas which does not condense under the conditions of flow to the gas condensing in the nozzle increases by a large factor the mass consumption of the condensing gas on passing through the nozzle. Thus dilution of N_2 with four times its volume of H_2 increased the density of the stream by a factor of 30. The addition of the noncondensing gas evidently facilitates condensation to the extent that it facilitates dissipation of the heat of association. The time required for attainment of the steady state was also estimated, and it was found that its order of magnitude agrees with that predicted by theory.

Henkes[176] used a mass spectrometer to detect the formation of aggregates in the apparatus of Becker, Klingerhofer, and Lohse[175]. He was able to detect aggregates containing up to 550 molecules in an H_2 stream. At the same time he established that the intensity of the electron beam bombarding the molecular beam being studied influences the distribution of the concentration of aggregates in the latter. Leckenby and coworkers[177] passes various gases and gas mixtures from a high-pressure cylinder into a mass spectrometer chamber through a nozzle with diameter 10^{-3} mm and established that aggregates of molecules are formed. When gas mixtures were used, the aggregates also consisted of different molecules. The concentration of aggregates was comparable with the concentration of monomeric molecules. An interesting feature is that for water vapour, aggregates with an even number of molecules were formed in larger quantities than the aggregates with an odd number of molecules. Greene and Milne[178] showed that the addition of 2.5% CO_2 to argon being passed through a nozzle into a mass spectrometer increases the ratio of the concentrations of monomer and dimer in argon by a factor of 3. The authors considered that this proves that the formation of the complexes is not due to the action of the ion source.

The determination of the concentration of aggregates in gases, even when these are not under supersaturation conditions, is of considerable interest for the verification of work on the calculation of the equilibrium concentrations of small aggregates. Bentley[179] used a combination of mass spectrometry and the Kundsen effusion technique to measure the concentration of associates of molecules in CO_2. He showed that the concentrations of the associates are given by power functions of the concentration of the monomer. In particular, he found that $C_2 \sim C_1$,[2,85] $C_3 \sim C_1$,[7,8] and $C_4 \sim C_1$.[11] Bentley showed that CO_2 contains aggregates of up to 23 molecules.

It has not as yet been possible to interpret quantitatively the results of mass spectrometric studies of the formation of nuclei. The attempt made by Dunning[180] cannot be regarded as successful, since he used macroscopic values of the surface tension and density in the calculation of the equilibrium concentrations of these small clusters.

Milne[181] compared the results of mass spectrometric determinations of the formation of dimers during the flow of argon through a molecular nozzle with calculations by the method of Storgyn and Hirshfelder[96] and obtained satisfactory agreement.

Spontaneous condensation during the cooling of a vapour–gas stream in a heat exchanger with turbulent flow was the subject of a theoretical and experimental study by Amelin[118,182]. An ultramicroscope was used to determine the mean dimensions and concentration of droplets of sulphuric acid and glycerol, and the results were compared with those obtained by a theoretical stepwise calculation. It was shown that when Frenkel''s equation is used, satisfactory agreement with experiment is obtained for glycerol, the experimental and theoretical values of the count concentration differing by a factor of not more than 3–4. For sulphuric acid, however, the results of calculations using the Becker–Doring equation gave better agreement with experiment.

A third method for achieving supersaturation in experiments on spontaneous condensation is by mixing streams of gases at different temperatures, with the hotter gas containing the condensing vapour, or by mixing hot vapour with a cold gas by molecular diffusion.

Spontaneous condensation during the mixing of streams at different temperatures was first studied by Fuks and Oschmann[183] and by Petryanov and Tunitskii[127], who used three-way capillaries for the mixing. The inadequate state of development of the theory of turbulent mixing at that time made it impossible to carry out a quantitative interpretation of the results obtained. Some important qualitative conclusions were reached in this work, however. In particular, it was concluded that with increase in the concentration of condensing vapour the rate of nucleus

formation does not increase indefinitely, but reaches a limiting value. Petryanov and Tunitskii[127] also concluded that in the condensation of the vapour of substances with low volatility and very low partial pressures, the formation of aerosols takes place by a coagulation mechanism. This is not always true, however, since Fuks and Sutugin[184], in a study of the condensation of NaCl vapour with a partial pressure of $\sim 10^{-7}$ mmHg, showed that when streams at different temperatures are mixed in a three-way tube, the concentration of the aerosol formed may be very low— $\sim 10^2$ cm^{-3}—and this excludes the possibility of a coagulation mechanism.

An elegant method for studying spontaneous condensation using an immersed turbulent stream was proposed by Amelin[185]. The method is based on the fact that the supersaturation in the mixing zone of the stream at first increases with dilution of the hot gas of the stream, reaches a maximum, and then decreases. By varying the temperature of the flowing stream and the medium, it is possible to achieve conditions under which the supersaturation will exceed the critical value only in a very narrow part of the mixing zone. The critical supersaturation of glycerol vapour[186] determined by this method was found to be close to that calculated by the Volmer–Flood formula. Higuchi and O'Konski[123], using an improved version of Amelin's method, showed that Frenkel's equation very effectively describes nucleation in dibutyl phthalate and glycerol vapours but describes that in sulphur vapour slightly less effectively. The agreement for triethylene glycol was poor, and the authors cited attributed this to the presence of impurities. It should be noted that in their comparison of experiment and theory, Higuchi and O'Konski compared the published values of the surface tension of the substances used with values calculated from experimental data on the rate of nucleation. Since J depends to a very marked extent on σ, there may be considerable discrepancy in J for good agreement in the values of σ. Sutugin and Fuchs[73] studied the condensation of silver vapour in a hot submerged stream of argon. They deposited the aerosols obtained, measured the weight of the deposit and its specific surface, and used these results to calculate the dimensions of the particles and their count concentration. The experimental results were compared with theoretical calculations carried out by means of a theoretical scheme which they developed, using Reed's method[44] to calculate the free energy of the nuclei and the Rosinski–Snow scheme[131] to calculate the coagulation growth of the particles. The partial pressure of silver vapour in these experiments amounted to 0.01–1 mmHg. The nuclei began to be formed in significant quantities at supersaturations of $\sim 10^5$. It was shown that the degree of dispersion of the aerosols formed at high supersaturations is determined by coagulation, accompanied by merging of the particles. It was also shown that the proposed scheme of calculation can be used to predict quantitatively the parameters of the aerosols formed.

Spontaneous condensation during the mixing of coaxial streams at different temperatures in the diffuser of a KUST instrument[187] was studied by Kogan[188] and Rybin[189]. Kogan[188] showed that the introduction of the molecules of various substances decreases the magnitude of the critical supersaturation in diiso-octyl sebacate vapour, in qualitative agreement with Neumann and Doring's conclusion that in binary mixtures the critical supersaturation should be different from that in the pure vapours of each component. Rybin[189] studied the spontaneous condensation of the vapours of a number of organic liquids with low volatility in a KUST instrument. By making use of the equations for the material and heat balances, he calculated the magnitude of the supersaturation achieved with complete mixing of the streams, assuming that mixing precedes nucleus formation, and neglecting the condensation of vapour on the walls during mixing. The values of J calculated from the equations of the classical theory were found to be smaller than the experimental values by several orders of magnitude.

Gen and coworkers[190] studied aerosols formed by the diffusion of aluminium vapour into a cold rarefied inert gas. It was found that the dimensions of the particles decrease rapidly at first with decrease in the concentration of the vapour, and then remain almost unchanged, that is the concentration of the particles at first increased, and then reached a limiting value. The concentration of particles for a given concentration of vapour increased with decrease in the pressure of the inert gas. Turkevitch[191] used an analogous method to study the condensation of silver vapour and showed that the degree of dispersion of the resulting aerosol is determined by coagulation. The increase in concentration with decrease in the pressure of the inert gas was attributed to an increase in the rate of diffusion of the vapour and hence an increase in the rate of cooling.

Higuchi and O'Konski[123] pointed out that it is possible to achieve supersaturation by chemical or photochemical reactions. It has not yet been possible, however, to find a reaction which would take place so rapidly that it would be complete before the start of condensation of the product. In the large number of experiments on the study of condensation with chemical reaction, the latter took place at the same time as nucleation, and the reaction was usually catalysed on the surface of the forming particles. These features make quantitative interpretation of the experiments difficult.

In summarising the examination of the results of the experimental study of spontaneous condensation, it must be accepted that the experimental data confirm the classical Volmer–Frenkel–Becker–Doring–Zel'dovich theory rather than the new Lothe–Pound–Hirth theory. It can also be stated that existing methods for calculating the processes of aerosol formation using the equations of the theory of spontaneous nucleus formation make it possible to predict the parameters of the resulting aerosols with sufficient accuracy for practical purposes.

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