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Present State of the Theory of Homogeneous Nucleation

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The present state of the theory of the spontaneous condensation of a supersaturated vapour is discussed, and modern methods for calculating the free energy of nuclei of the new phase are examined, especially in the light of the resolution of the Lothe-Pound paradox. Reasons for the differences between the best known formulae for the rate of nucleation ara analysed. The limits of applicability of the existing theory to practical calculations are deduced from a consideration of a large quantity of experimental data, and specific problems that have not yet been completely solved are mentioned. A list of 179 references is included.

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I. INTRODUCTION

Many theoretical and experimental studies have been made on nucleation in a supersaturated vapour, both because of the fundamental importance of the kinetics of phase transitions of the first kind and because of the need to establish methods for engineering calculations on bulk condensation, which are required in many branches of technology. During recent years considerable progress has been made in this direction. In the theory of nucleation inaccuracy has been revealed in the Lothe–Pound concept, new methods have been established for calculating the bonding energy of small nuclei, and the mathematics of the theory has been improved significantly. New methods have appeared for studying nucleation–molecular beams, improved diffusion cells, and apparatus for investigating condensation during turbulent mixing—and laser techniques have been widely employed for tracing the

growth of the disperse phase. Condensation from the vapour has been studied on a greater range of substances. New methods for calculating bulk condensation have been developed. The present Review summarises and analyses these achievements.

II. KINETICS OF FORMATION OF A NEW PHASE IN A SUPERSATURATED VAPOUR—GENERAL APPROACH

Almost all current theories of the formation of a new phase from a supersaturated vapour are based on the so called Szillard model, according to which a supersaturated vapour comprises a mixture of monomeric molecules and molecular aggregates (clusters) containing different numbers of molecules. Clusters are able either to vaporise or to grow by adding molecules and finer clusters. The mathematical description of this model is based on the so called quasi-chemical approximation, which regards clusters of each size as chemical compounds characterised by definite free energies of formation from the monomer. Such an approach is rather unsound logically since, as will be shown later, calculation of the free energies of formation of clusters requires that the partition function of the system shall be expressed as a combination of small partition functions written for clusters of each size. Yet statistical thermodynamics should describe a system in a state of true—not metastable—equilibrium, and its application to a system whose parameters of state represent a region lying between the binoidal and the spinodal should give Maxwell's phase rule, as was demonstrated by Kac et al.[1] The statistical-mechanical formulation in current nucleation theory is therefore largely arbitrary and approximate, with the closeness of its approximation diminishing as the system moves from the binoidal towards the spinodal.

The purpose of nucleation theory is to predict the rate I of formation of stable particles of the condensed phase per unit volume of the supersaturated vapour under given external conditions, and also to determine the size at which these particles become stable. The free energy of formation of clusters ΔG_g increases with size for very small clusters, then passes through a maximum, and decreases to negative values. Clusters of size corresponding to the maximum free energy are said to be "critical", and are equally likely to grow or to vaporise. Nuclei characterised by negative free energies are completely unstable and capable only of growth. Such a system, corresponding to the Szillard–Farkas scheme, can be described by an infinite series of differential equations:

$$\frac{\mathrm{d}f_g}{\mathrm{d}t} = \frac{1}{2}\sum_{k=1}^{g-1}\beta_{g-k,k}f_{g-k}f_k + \sum_{k=g+1}^{\infty}\alpha_{k-g}^{k}f_k - f_g\left(\sum_{k=1}^{\infty}\beta_{gk}f_k + \frac{1}{2}\sum_{k=1}^{g-1}\alpha_{g-k,k}^{g}\right), \quad (1)$$

where f_g is the concentration of clusters comprising g molecules, β_{ij} is the probability of formation of a cluster of size g by the collision of i and j molecules, and α_{ij}^{g} is the probability that a cluster of size g will break down into clusters of sizes i and j.

It is useful for the subsequent discussion to distinguish two extreme cases of nucleation, which, following Gerlach[2], we shall term "rapid" and "slow" nucleation. Contemporary literature refers more often to condensation at high and at low supersaturations of the vapour S, but this seems less appropriate, since it is difficult to choose a criterion for assessing supersaturation. The absolute supersaturation means nothing by itself, since for different substances and under different conditions the same supersaturation may correspond to rates of nucleation, i.e. rates of formation I of nuclei of supercritical size, differing by several powers of ten. Nor can the critical supersaturation S_{cr}, corresponding to $I = 1$, be regarded as significant, since it may vary over a similarly wide range as the temperature changes from the absolute zero to the critical point, with the character of nucleation at a constant rate I also varying with temperature. It is advisable to use the degree of reversibility of migration of a cluster along the size (g) axis as a measure of the rapidity of condensation. White showed[3] that under steady-state conditions the mean time required for a cluster to pass from the point $g = 1$ into the supercritical region is f_1/I. A dimensionless parameter for the rapidity of nucleation can be obtained by dividing this quantity by the time of collision between molecules of the vapour at zero time $\beta_1 f_1^0$. The resulting parameter $\theta^* = f_1^2\beta_1 I^{-1}$ has values of 10^{22}–10^{28} for the condensation of water or alcohol vapour in Wilson cloud chambers (typical cases of slow nucleation) and only 10^3–10^4 for the condensation of the highly dilute vapours of inorganic substances.

Rapid condensation is characterised by small (<10) critical nuclei, a sharp decrease in the free energy of formation of clusters in the supercritical region (so that the addition of one molecule to a critical cluster is equivalent to falling into a trap), and a considerable role of collisions between clusters. In slow condensation the critical nucleus contains several tens of molecules, and clusters grow by adding single molecules of the monomer (provided that the vapour is not already associated in the unsaturated state). It is significant also that processes of the rapid type overlap in time with the coagulation of supercritical particles, whereas slow processes are separated in time from subsequent coagulation. Slow nucleation usually occurs in relatively dense vapours (and partial pressures >0.1 mmHg), but rapid nucleation at low vapour densities, since in the latter case condensation during supersaturation is unable to diminish its extent significantly. Difficulties are involved in describing both types of processes. Thus with rapid nucleation the free energy ΔG_g cannot be expressed in terms of parameters of macroscopic quantities of the condensed phase, since such processes are usually accompanied by change in the external conditions. Slow nucleation takes place at a temperature comparable with the critical point, leading to thickening of the interfacial layer on the nuclei and making it difficult to describe their properties. The concentration ratio of the carrier gas to the vapour is far greater in rapid than in slow nucleation, which ensures the isothermal character of the process and the relaxation of the distribution of energy between degrees of freedom of the cluster in the time intervals between successive collisions between it and molecules of the vapour.

The greatest attention has hitherto been paid to slow nucleation in a monomolecular vapour with the concentration of the monomer maintained constant. A considerable number (>30) of formulae have been suggested for the rate I under steady-state conditions, which makes it difficult to choose an expression for the analysis of experimental results or for engineering calculations. We shall therefore repeat the deduction of the formula for the rate of nucleation, incidentally mentioning the sources of discrepancies between the results of different authors and examining individual attempts to improve the theory.

The migration of nuclei along the size axis, caused by the addition or the evaporation only of individual molecules, is described by the equation

$$\frac{df_g}{dt} = I_{g+1} - I_g, \tag{2}$$

where I_{g+1} is the number of nuclei passing in unit time fro from the point g to the point $g + 1$, which can be expressed

$$I_g = \beta_{g-1} f_1 g_{g-1} - \alpha_g f_g. \tag{3}$$

The set of equations (2) in principle enables the distribution $f_g(t)$ to be determined at any time provided that formulae are known for α_g and β_g.

We shall now make certain general statements, whose validity is independent of the specific form of α_g and β_g. Firstly we consider the steady-state process, when f_g is independent of t, so that I is independent of g. We rewrite (3) in the form

$$I = -\alpha_{g-1} f_{g-1} + \beta_g f_g f_1 \tag{5}$$†

which represents a set of inhomogeneous linear equations in f_g. In order to find I, we first solve the homogeneous equation

$$\alpha_{g-1} c_{g-1} - \beta_g f_1 c_g = 0 \tag{6}$$

when we have

$$c_g = \prod_{j=2}^{g-1} \frac{\alpha_{j-1}}{\beta_j}. \tag{7}$$

Supposing that $I \neq 0$, we find $f_g = A_g c_g$, where A_g is determined from (5) by the recurrence relation

$$A_g = -I \sum_{s=2}^{g} (\beta_s f_1 c_s)^{-1}. \tag{8}$$

If we put $g = 2$, we have $A = f_1$, so that

$$f_g = c_g \left[f_1 - I \sum_{s=2}^{g} (\beta_s f_1 c_s)^{-1} \right]. \tag{9}$$

The next problem is to find I, which usually involves the assumption that sufficiently large clusters are removed from the system, i.e. that $f_G = 0$ at some point G. From (5) and (9) we then have

$$I = \left[\sum_{s=1}^{G-1} (f_1 \beta_s c_s)^{-1} \right]^{-1}. \tag{10}$$

Combining (9) and (10) gives

$$f_g = c_g I \sum_{s=g}^{G-1} (f_1 \beta_s c_s)^{-1}. \tag{11}$$

Formulae (10) and (11) relate I and f_g to the coefficients α_g and β_g.

The next step should be to express I and f_g in terms of parameters defining the state of the vapour and the properties of the substance, and to transform the sums occurring in these expressions. This would require that the concentrations c_g, which would be maintained in the vapour in the absence of a flux of nuclei along the g-axis, should be identified with the equilibrium concentrations determined from the condition of equality

$$\mu_g = g\mu_1. \tag{12}$$

of the chemical potentials μ_g of the same quantities of substance included in clusters of different sizes. We again recall that this is strictly valid only for equilibrium association in an unsaturated vapour: the soundness of such identification becomes increasingly dubious with deeper penetration into the region of metastable states. Since μ_g can be written as the sum of the standard chemical potential μ_g^0 and the concentration-dependent term $kT \ln c_g^*$ (where c_g^* is determined by some concentration adopted as standard), c_g can be expressed in terms of f_1 and the Gibbs free energy of formation of the cluster $\Delta G^* = \mu_g^0 - g\mu_1^0$:

$$c_g = f_1 \exp(-\Delta G^*/kT). \tag{13}$$

The Kelvin–Gibbs equation is usually employed to express ΔG^* in terms of the surface tension σ and the density ρ of the condensed phase. Logical difficulties associated with this step will be discussed later. Replacing the summation in formula (10) by integration, we obtain for the rate of nucleation

$$I = \left(\int_0^G \frac{dg}{f_1 \beta_g c_g} \right)^{-1}, \tag{14}$$

(where G is the size of the clusters for which $f_g = 0$), which can be used for the direct calculation of I.

Frenkel'[4] and Zel'dovich[5] replaced the set of difference equations (3) by the equation of diffusion along the g-axis in order to calculate the rate of nucleation. Becker and Döring[6] resorted to direct replacement of the sum (10) by the integral, using the equation $\alpha_{g^*} = \beta_{g^*}$ instead of (6), which entailed an inaccuracy from disregard of the change in surface area of the particle on the vaporisation from it of one molecule, and led to a result differing from that of Frenkel' and Zel'dovich by a factor of $g^{-2/3}$. As shown both by Barnard[7] and by Petrovskii and Amelin[8], when the correct condition (6) is used, the Becker–Döring procedure gives a result identical with that of Zel'dovich and Fenkel'. It may be mentioned here that the difference between Barnard's[7] and the Becker–Döring results is due to the retention by the former, after replacing the sum $\Sigma g^{-1/3}$ by the integral

$$\int g^{-1/3} dg = \frac{3}{2} g^{2/3} - 1 \tag{15}$$

of unity, which undoubtedly improves the accuracy, since replacing a sum by an integral by itself introduces an inaccuracy of the same order. Indeed, White's deduction[3], based on a consideration of discrete migrations along the g-axis and not involving replacement of summation by integration (or other approximate operations), gives precisely the same numerical values of I as do Frenkel'–Zel'dovich calculations. The final calculated result (for steady-state conditions) can be written

$$I = [f_1 \exp(-\Delta G^*/kT)]\,[f_1 \beta_{g^*}]\,Z, \tag{16}$$

where the three factors in square brackets are the equilibrium concentration of nuclei of critical size c_{g^*}, the rate of condensation of the vapour on the critical nuclei, and the so called Zel'dovich factor, which allows for the fact that the concentrations f_g do not reach the equilibrium values c_g. All three quantities are expressed in terms of phenomenological parameters. For ΔG^* we have

$$\Delta G^* = 4\pi r^{*} \sigma, \tag{17}$$

† The Russian version contains no Eqn. (4) (Ed. of Translation).

where the radius r^* of a critical nucleus is found from the condition $d\Delta G/dr = 0$:

$$r^* = \frac{2\sigma M}{kT\rho N \ln S}; \quad \Delta G^* = \frac{16\pi\sigma^3 M^2}{3(kT\rho N)^2 \ln^2 S} \tag{18}$$

in which M is the molecular weight, N Avogadro's number, and S the supersaturation. The rate of growth is found by combining (18) with Knudsen's formula:

$$\beta_{1g} f_1 = \frac{\gamma_g f_1 kT}{(2\pi mkT)^{1/2}} \cdot 4\pi r^{*2}, \tag{19}$$

where γ_g is the condensation coefficient and m the mass of the molecule. Finally, for Z we have

$$Z \equiv (f_g/c_g) = (\Delta G/3kT\pi g^{*2})^{1/2} = \frac{\rho \ln^2 SN}{8\pi M}\left(\frac{kT}{\sigma}\right)^{3/2} \tag{20}$$

from which it follows that $Z \simeq 0.01$. Substituting (18)–(20) in (16) yields the Frenkel'–Zel'dovich formula for the rate of nucleation:

$$I = 9.6 \cdot 10^{25} \frac{\gamma}{S\rho} f_1^2 \left(\frac{2M\sigma}{\pi N}\right)^{1/2} \exp\left[\frac{16\pi}{3}\left(\frac{\sigma}{kT}\right)^3 \left(\frac{M}{\rho \ln S}\right)^3\right]. \tag{21}$$

The same (or very similar) expressions were obtained by independent methods by Gerlach[2], by Deryagin[11,12], and in papers already cited[8,9]. Equation (21) is based on the hypothesis that clusters can be regarded as spherical droplets possessing the macroscopic density and surface tension. Some inaccuracy, slight in the case of slow nucleation, is introduced by the use of Knudsen's formula, while the β_{1g} should be expressed as coefficients of the frequency of collision between gas molecules (since clusters must be regarded as molecules of a Lorentzian gas).

Equation (16) applies also to rapid nucleation when occurring under steady-state conditions, and the expressions for Z obtained from a consideration of discrete migrations along the g-axis are equally applicable to the two types of nucleation. Accurate calculations[9,10] show that Z for rapid nucleation is close to unity and in any case at least 0.5. The difference from unity can safely be neglected because of the relative inaccuracy of the determination of ΔG. However, proof of the validity of the formulae for Z in the case of rapid nucleation is essentially of value merely to illustrate the possibility of a common approach to the description of nucleation, since rapid nucleation is usually accompanied by rapid changes in the temperature and the concentration of the vapour, which makes the use of steady-state solutions impossible. The description of nucleation must then be based on the numerical solution of equations of type (2) by means of an electronic computer[13,14].

It must be noted here that with rapid nucleation the cluster concentrations may differ very markedly from the equilibrium values for the instantaneous temperature and monomer concentration. This may be because for small g the condensation coefficient may be strongly dependent on the cluster size and change significantly when g decreases even by unity. According to Gerlach[2] it is sufficient that

$$(\Delta G_{g^*} - \Delta G_{g^*-1})/kT > 3 \tag{22}$$

in order that Z should be close to unity (disregarding the dependence of γ on g). This condition (22) becomes insufficient when $\gamma(g-1) \ll \gamma(g)$. However, another simplification is possible in this case: with $Z \ll 1$ the possibility of the vaporisation of molecules from the clusters can be neglected, which removes the necessity of solving the complicated problem of determining the free energies of small clusters.

The Reviewers' numerical calculations on rapid condensation[15,16] showed that, after some time θ^* ($\sim 10^3$ in $\beta_1 f_1^0$ units), the monomer becomes completely exhausted, and the subsequent course of the size distribution of condensed particles is governed by coagulation. An asymptotic regime is established, in which the particle concentration decreases with time according to a $t^{-6/5}$ law, as was predicted by Lai et al.[17], and also by Lushinkov[18] for purely coagulation processes (i.e. for systems in which every collision of monomeric particles results in their association with 100% probability).

The quantity θ^* depends on the type of relation between γ and g or on the free energy of formation of the clusters, but never exceeds 10^4 for rapid condensation: independly of its value, the subsequent evolution of the coagulating system follows the same $t^{-6/5}$ variation, with the mean particle size depending unambiguously on the dimensionless time

$$\theta = \beta_{11} f_1^0 t. \tag{23}$$

If the temperature of the system and the concentration by weight of the vapour vary, this quantity is given by[19]

$$\theta = \beta_1 f_1^0 \int_0^t F(t') T^*(t')\, dt', \tag{24}$$

where

$$F(t') = \Sigma g f_g / f_1^0$$

is the time variation of the concentration of the condensing substance and

$$T^*(t') = \sqrt{T(t')/T_0};\ T_0$$

in which T_0 is the temperature at zero time. Knowledge of θ permits immediate determination of the number concentration, the preceding particle size, and the size distribution[17–19].

Ultimately, of course, the existence of any gas-disperse system always ends in coagulation, but with slow nucleation the quantity θ^* usually exceeds greatly the lifetime of the system.

III. GROWTH AND VAPORISATION OF CLUSTERS

Following the ideas of Gibbs, the classic theory of nucleation assumes that the free energy of formation of a cluster can be written

$$\Delta G = 4\pi r^2\sigma - kT \ln S = ag^{2/3} - (\mu_v - \mu_l) g, \tag{25}$$

where μ_V and μ_l are the chemical potentials of the vapour and of the condensed phase. The second term in (25) can be expressed in terms of σ by means of the well known Kelvin–Gibbs formula

$$kT \ln S = \frac{2M\sigma}{N\rho r}, \tag{26}$$

which also gives an expression[18] for ΔG. This was used for many years in the theory of nucleation, until a few years ago the criticism by Lothe and Pound[20–23] and also by their successors[24–26] cast doubt on the hitherto orderly set of ideas. The arguments of these authors changed from paper to paper under the influence of counter-arguments, but the general sense of the proposed revision of the classic theory was invariably that formula (25) describes the free energy of a drop having a fixed centre

of mass, but not that of a nucleus endowed with external degrees of freedom and undergoing thermal motion in the space occupied by the condensing system.

In order to examine this question in detail, we must pass to the statistical-mechanical description of a multicomponent gas comprising a mixture of monomeric molecules and molecules aggregates of various sizes. The phase integral for such a mixture can be written

$$Q = \frac{1}{N!h^{3N}} \int \mathrm{d}^{3N} \boldsymbol{P} \int \mathrm{d}^{3N} \underline{r} \exp\left\{-\beta\left[\sum_i \frac{P_i^2}{2m} + U(r_1 \ldots r_N)\right]\right\}, \qquad (27)$$

where P is the momentum of the molecule, U is the potential energy of interaction among all the molecules present, and $\beta = kT^{-1}$. We now express (27) in terms of the configurational partition functions for the individual nuclei, in which integration with respect to the coordinates is performed only over some bound region C, where each nucleus exists as a single bound group of particles:

$$q_g = \frac{(2\pi mkT)^{3g/2}}{g!h^{3g}} \int_C \exp[-\beta U_g]\, \mathrm{d}^{3g}x, \qquad (28)$$

in which U_g is the energy of interaction of the molecules in a cluster.

The change to integration over bound regions itself causes discrepancies and, in the opinion of several authors, should be accompanied by the introduction of correction factors. However, the chief source of discrepancies is the mode of expressing q_g in terms of ΔG_g. If the chemical potential of a nucleus can be expressed

$$\mu = kT[\ln(q_g/N) - \ln(c_g/N)], \qquad (29)$$

it follows from the smallness of the difference between the Gibbs and the Helmholtz free energies that

$$c_g = q_g \exp(g\mu_1/kT). \qquad (30)$$

According to Lothe and Pound the quantity

$$\lambda_g = \exp(-G_g/kT);\ G_g = \Delta G + g\mu_1, \qquad (31)$$

is not identical with q_g but is a partition function for a spherical volume isolated in the massive liquid, occupied by g molecules, and provided with an interface. If in (30) we then use λ_g instead of q_g, we must introduce the correction factor

$$\Gamma = \frac{1}{N}\left\{\frac{q_g^{tr} q_g^r}{\lambda_g^{tr}\lambda_g^r}\right\}, \qquad (32)$$

termed[20-23] the "replacement factor", in which q^{tr} and q^r are the partition functions for the collective rotational and translational motion respectively of the nucleus, and λ^{tr} and λ^r are the corresponding partition functions for the spherical volume regarded as a drop with a fixed centre of mass. (The term "replacement factor" is sometimes applied to the product $\lambda_g^{tr}\lambda_g^r$.) Estimates of Γ based on reasonable values for the vibrational spectral parameters of the molecules in the liquid and for the moments of inertia of the nuclei give a correction of $\sim 10^{17}$ to the rate of nucleation.

Reiss and his coworkers[27-29], Lin[30], Stillinger[31], and also Rusanov and Kuni[32,33] correctly pointed out that the volume of liquid cannot be regarded as a drop with a fixed centre of mass, and that it is more correct to regard it as a drop having fixed boundaries. Because of the ability of the centre of mass of such a drop to fluctuate within its boundaries the replacement factor decreases to comparatively low values depending on the method used to estimate these fluctuations. On the basis of the earlier general theory of equilibrium in polydisperse systems[32] Rusanov and Kuni[33], as well as Parlange[34], showed that the difference between the free energies of formation of a freely moving drop and of a drop having fixed boundaries is almost equal to the difference between those of a mobile nucleus and of a drop having a fixed centre of mass. Certain analogies that can be drawn between the concepts of nucleation theory and those of nuclear physics indicate that the two models—a drop with fixed boundaries and a free nucleus--are in general identical, i.e. that $\Gamma = 1$. The model with fixed boundaries is indeed analogous to the shell model of the atomic nucleus, while the model of a free nucleus is analogous to the drop model. The identity of these models of the atomic nucleus has been demonstrated[35], at least at high temperatures.

In order to obtain agreement between calculated and experimental equations of state[36,37] the value of σ corresponding to the free energy of a planar surface per molecule must be replaced in (18) by values about 10% larger. Thus the surface tension must be correspondingly overstated in isolating the contribution of the collective motion of the cluster.

In the case of a fixed centre of mass ($\lambda_g^{tr} = 1$) the introduction of a replacement factor (allowing only for translational motion) is equivalent to multiplying q_g by $h^3/(2\pi gmkT)^{3/2}$. This view was most clearly expressed by Abraham[23], who, having isolated in the Hamiltonian of the nucleus the components corresponding to the collective translational and rotational motion, diminished by six the number of internal degrees of freedom over which the summation was made. From the equality of molecular momenta in gaseous and liquid phases at a given temperature Bashkirov and Sutugin have shown[38] that the restriction $\Sigma \mathbf{P}_g = \mathbf{P}$ is imposed on the range of integration in the evaluation of the phase integral over the components of the collective momentum from the momenta of the individual molecules constituting the cluster. The isolation in q_g^{tr} of a factor exceeding $g^{9/2}$ times the partition function for three internal degrees of freedom should then entail the division by $g^{9/2}$ of the partition function for the internal degrees of freedom. It is noteworthy that this approach was made by Frenkel' (though without comment) when, speaking of the need to allow for external degrees of freedom of the clusters, he replaced g by $g - 2$ in both terms of Eqn. (25). The Lothe–Pound approach is equivalent to substituting $g - 2$ only in the volume term. The equality of molecular momenta in liquid and gaseous phases in general supports the identity of the partition functions of the cluster and of a volume isolated from a liquid and provided with a surface: i.e. it indicates that formula (25) reproduces correctly the free energy of formation of a cluster whose physical properties coincide with those of a drop. However, several authors consider[31,39,40] that the configurational parts of the phase integrals for the cluster and for the volume isolated from the liquid differ somewhat, and there is also no unanimity on the magnitude of this difference. As already stated, however, the replacement factors obtained from the estimated configurational integrals are by no means so large as in the papers by Lothe and Pound.

A final comment on the replacement factor is that the Lothe–Pound approach leads to the conclusion that the concentration of free clusters in equilibrium with a given monomer concentration should far exceed the concentration of drops having a fixed centre of mass. Hence isothermal distillation of matter should take place from

stationary to moving drops, which is obviously inconsistent with the law of the conservation of energy. The same argument can be used also in refutation of the identity of a cluster and a volume isolated from the liquid[38].

It is interesting[29,41] that in one case the replacement factor may indeed differ markedly from unity—in the formation of rigid spherical nuclei and molecules possessing non-degenerate rotation—when the factor should by less than unity. The possibility of the formation of solid, not supercooled liquid, nuclei from the vapour has not yet been proved; moreover, an aggregate of 20–90 molecules cannot be regarded as a smooth, rigid sphere.

The immense values of the Lothe–Pound replacement factor gave rise to many hypotheses on the nature of clusters to explain the discrepancy between the theory and experiment[42-47]. Since the Lothe–Pound theory is now obviously untenable, we shall not discuss these hypothesis further.

Two sources of uncertainty arise in connection with the coefficients β_g. Firstly, the density of clusters would be smaller than the macroscopic value ρ (see Section IV), so that the surface area of a cluster should be greater. Secondly, information is lacking on the coefficient of condensation $\gamma(g)$ on small clusters. It has been stated repeatedly that γ may diminish appreciably with decrease in size of the clusters. As long as we consider isothermal condensation (i.e. suppose that all the heat evolved in the system is immediately absorbed by the thermostat), however, it follows from the principle of detailed balancing that condensation and evaporation coefficients are equal. This implies that a decrease in γ should not affect the steady-state rate of nucleation, since from Eqns. (3), (5), and (6) we have

$$f_g = \frac{\beta_1\beta_2 \dots \beta_{g-1}}{\alpha_2\alpha_3 \dots \alpha_g} c_g, \tag{33}$$

and such coefficients occurring in β and α cancel out. Under completely isothermal conditions the decrease in γ with small clusters can affect only the time required to attain a steady state after the instantaneous establishment of supersaturation in a system comprising monomeric molecules. In practice the removal of heat of condensation is never instantaneous, which would influence significantly the course of elementary processes involving the smallest clusters, as the efficiency of collisions between vapour molecules and clusters drops sharply. Since the evaporation coefficient is an intrinsic property of the actual cluster, it is unaffected by non-isothermal conditions, and with small values of g the decrease in γ will lead to a decrease in I_0. These effects will be discussed in detail in Section VI.

Okuyama and Zung[48] tried to obtain an analytical expression for the dependence of γ on g. They started from the fact that γ should decrease with increase in the positive curvature of the surface, since the condensation of a molecule on a drop must involve work to increase the surface of the latter. However, one of the Reviewers has pointed out[49] that this is already taken into account by the Kelvin–Gibbs formula, and the Okuyama–Zung result is incorrect. The erroneousness of the latter formula is readily illustrated by applying it to condensation on a concave meniscus, when values of γ exceeding unity are obtained.

IV. PROPERTIES OF SMALL CLUSTERS

The evident doubt as to the applicability of phenomenological parameters, relating to major quantities of the condensed phase, to express the free energy of formation of clusters has stimulated a search for other methods of determining this function. The first attempts of this kind were based on the use in expressions for ΔG of surface tensions for a curved surface. A considerable number of such papers, reporting essentially modifications of Tolman's theory of surface tension, were surveyed in a previous review[50].

The one-sided character of these attempts was shown[51-54] by the demonstration that the decrease in tension of the curved surface of a cluster is accompanied by an increase in thickness of the interfacial layer with a consequent decrease in density of the droplets. Study of the asymptotic behaviour of the configurational integral of liquid droplets showed[55-57] that the free energy of a cluster cannot in general be written in the form $ag + bg^{2/3}$ and that expressions for ΔG should contain terms proportional to $g^{-1/3}$, $\ln g$, and—what is especially important—a term representing the contribution by capillary waves. It was also revealed[57] that the theory of the tension tensor in the interfacial layer, usually employed to determine the dependence of σ on surface curvature, is completely unable to reproduce the significant properties of clusters.

Decrease in the size of a cluster is not simply accompanied by a decrease in its density: the radial distribution of density in a cluster depends on its previous history and on the degree of saturation of the vapour—a conclusion reached by Strickfaden and de Sobrino[58], who calculated the density profile as a solution of the diffusion equation for molecules in the self-consistent field of the cluster.

Considerable efforts were concentrated on attempts to express ΔG in terms of the parameters of the intermolecular interaction potential for the molecules forming the cluster. Regarding a cluster as a polyatomic molecule, we can write

$$q_g = q_{tr}q_r q_v q_0, \tag{34}$$

where q_{tr}, q_r, and q_v are the translational, rotational, and vibrational partition functions respectively, while $q_0 = \exp(-U_0/kT)$, in which U_0 is the minimum potential energy of the cluster. If the cluster comprises polyatomic molecules, a factor must be included to allow for the contribtuion by intramolecular degrees of freedom. The main difficulties in solving such a problem are to determine moments of inertia, the set of frequencies, and the bonding energy. It is first necessary to assign a definite structure to the cluster; thus this approach is applicable only to crystalline nuclei. Yet several workers consider that direct formation of crystal nuclei from a vapour is impossible, since clusters are amorphous according to Ostwald's rule, and are able to crystallise only when they have become much larger than the critical size[59,60].

The first reported determination of q_g was made by Reed[61], who calculated it for nitrogen clusters on the assumption that the interaction of molecules in a cluster is described by a Lennard–Jones potential with clusters of each size existing in the most stable configuration (as dumbbells, regular triangles, tetrahedra, double tetrahedra, and cubes respectively). This method was modified by Andres[62] for clusters up to $g = 12$. Later papers specified only the lattice type, and interatomic distances were determined by finding the minimum potential energy.

Such calculations were made for argon clusters by Burton[63-65] and by McGinty[66], who both calculated the rate of nucleation by means of formula (14) and obtained agreement with calculations based on the classical theory and the surface tension of solid argon. In contrast to the classical theory, quantum-mechanical calculations predict several characteristic properties for clusters, e.g. an anomalous size dependence of heat capacity, and a non-monotonic dependence of q on g. Abraham and Dave[67-69] showed that results identical with those of Burton and of McGinty can be obtained more simply by calculating the thermodynamic properties of crystalline clusters by means of the Einstein theory of the heat capacity of crystals extended to a system bounded by an interface.

Burton's most recent calculations[70] of rates of nucleation in argon vapour, based on quantum-mechanical calculations of ΔG, differ markedly from the predictions of the classic theory: over the range of supersaturations 12–72 and at reduced temperatures of $T/T_{cr} = 0.35–0.47$ the ratio of his values of I to the classical values increases from 10^{-2} to 10^{7}. Bonissent and Mataftschiev[71] made similar calculations for an arbitrary model substance whose molecules interacted in conformity with a Lennard-Jones potential. Having calculated the equilibrium concentrations of hexagonal clusters of 2–14 atoms, they also computed the surface tension for crystals of the same model molecules, and from this latter value found the classic equilibrium concentrations. Good agreement was found between such pseudoclassical calculations and rates of nucleation calculated in terms of the intermolecular interaction potential. These authors concluded that the possible existence of different configurations of the clusters does not affect significantly the values of c_g, but Burton[70] holds the opposite view.

It is interesting that the process of selecting configurations for clusters by successive approximation to the configuration corresponding to minimum free energy involves significant distortion of the lattice assigned *a priori* to the clusters. Use of the Lennard-Jones potential yields especially considerable distortions of crystal structure for $g = 13$ and 55.[72] Use of the Morse potential in the calculations encountered the same difficulty[73-75]. It was concluded that this problem is complicated by taking long-range forces into account, and this is what prevents the application of quantum-mechanical calculations to clusters containing >100 atoms.

The impossibility of achieving crystalline structures in clusters is probably the reason for the frequent observation of amorphous disperse condensates. This supports the concept[76] that subcrystallites consisting of a few atoms appear before particle formation. A cluster formed from such subcrystallites cannot have a crystalline structure.

Quantum-mechanical calculations for molecular aggregates in the vapours of several metals[77] do not give good agreement with experimental results even for a dimer: adjustment with the aim of improving agreement for the bonding energy increases the divergence of vibration frequencies, and conversely. Nevertheless, these results were used for calculations of bonding energy in Ag_g and Pd_g complexes, for which great stability of linear and cyclic aggregates was predicted in comparison with aggregates having a three-dimensional structure[78].

Relatively numerous attempts have been made to calculate aqueous clusters. Inspection of results obtained by various workers[79] indicates that the properties of the dimer can be calculated quite well. Large clusters, however, exhibit discrepancies both in quantitative estimates of bonding energy and in the determination of the relative stability of linear and cyclic structures. Del Bene and Pople[80] found that cyclic clusters are the more stable, supporting this conclusion by the presence at 3.5 Å in liquid water of a maximum in the radial density distribution function, a position which can be interpreted as the distance along the diagonal in the cyclic tetramer[81]. Recalculation of cyclic clusters[82] suggested absence of the non-additivity of bonding energy which might have been responsible for their great stability, so that linear aggregates should be the more stable, the correctness of the calculation being illustrated by prediction of the true bonding energy of ice. The linear structure of water complexes is suggested by experimental observations[83] on the magnetic focusing of beams of molecular aggregates.

Plumer and Hale[84] calculated clusters containing up to 57 H_2O molecules, and arbitrarily chose a cyclic pentamer as unit cell. They assumed that a cluster has an ordered structure, as indicated by the existence of hydrogen-bonded complexes in liquid water. Nevertheless, the Hagler–Scheraga–Nemethy theory of the structure of liquid water[85] in fact interprets water as a mixture of clusters of different sizes, but the maximum in the size distribution function occurs at $g = 4–5$, and clusters larger than 50 molecules are completely absent from the liquid phase. A nucleus in the vapour phase, consisting of tens of molecules, is therefore also more logically regarded as a complex of smaller clusters of hydrogen-bonded molecules bound together by van der Waals interactions. The values obtained[84] for ΔG are scattered on both sides of the classic $\Delta G–g$ curve. This scatter would obviously have been diminished by taking into account the existence of a large number of ruptured hydrogen bonds in the cluster.

The possible existence of different geometrical configurations for clusters of a given size makes it necessary to consider the statistical contribution made to q_g by each configuration. The growth of clusters under such conditions should be regarded, strictly speaking, not as unidimensional diffusion along an axis but as displacement in a multidimensional space. Ziabiki[86] deduced a multidimensional kinetic equation of nucleation, the dimensions of which were equal to the number of faces on the cluster–nucleus. Semenchenko and Petrovskii[87] were able to reduce this equation to a one-dimensional form by using Semenchenko's thermodynamic theory of small crystals[88], enabling ΔG to be expressed in terms of the Wulf constant. In the view of these workers anisotropy of the crystal nucleus should have little effect on the magnitude of ΔG.

Equilibrium concentrations of dimers have been calculated not only in Refs. 61 and 62 but also in Ref. 89, in which the Morse potential was used for argon and krypton. The dynamic equilibrium in a system containing monomeric and dimeric molecules has been examined[90]: the concentrations of three types of bound states—stably bound, metastably bound, and dissociating—were calculated for various gases over a wide temperature range by use of the rectangular-well and Sutherland potentials. The temperature dependence of c_2 obtained at low temperatures was closely similar to the results of calculations by Reed's method[61], but the discrepancy increased with rise in temperature. Divergence between results in Refs. 89 and 90 was slight. In a monomer–dimer system not in contact with a thermostat the temperature of the dimer is below, while that of the monomer is above, the average temperature of the mixture[91]. Even when this effect is taken into account, however, the concentration of dimers is similar to that calculated by Stogrin and Hirschfelder[90].

V. NUCLEATION UNDER NON-STATIONARY CONDITIONS

Two cases of non-stationary nucleation can be distinguished: either supersaturation is established instantaneously and then remains constant, or it varies continuously throughout the process. A steady state may be established in the former case, but some time is required for the concentrations to become steady, and during this period the rate of nucleation will increase from zero to the steady value I_0. Several workers investigated the time of attainment of a steady state[92-96] by solving the time-dependent equation for the diffusion of nuclei along the size axis with the initial conditions $c_1 = 1$ and $c_g = 0$ with $g \neq 1$. The rate of nucleation under non-stationary conditions was shown to be related to the steady value:

$$I(t) = I_0 \exp(-\tau/t), \tag{35}$$

where

$$\tau = A(\beta_1 c_1 S_g)^2 Z,$$

is the relaxation time of nucleation, in which A is a numerical coefficient estimated by various authors to lie within the range $\frac{1}{4}(1-\pi)$.

Abraham[97] used a computer to solve Eqns. (2) with the aim of studying non-stationary nucleation at a constant supersaturation S, and his results indicated the analytical solution in Refs. 95 and 93 to be the most accurate. Similar values of τ were obtained[98] in a numerical tabulation of the solution of the equation of non-stationary diffusion in quadratures. Computer calculations by Courtney[92] indicated rather slower establishment of a steady state, probably because of his use of a different expression for c_g.

Abraham also investigated the effect of the cluster-size dependence of the condensation coefficient on the time of establishment of the steady state. Although the erroneous Okuyama–Zung formula[48] for the γ–g dependence was used in these calculations, the results give an idea of the possible influence of this factor. According to Abraham's calculations[99] the concentration of clusters considerably smaller than the critical size approaches steady values, passing through a maximum; the concentrations of clusters of near critical sizes increase monotonically to steady values.

If the change of supersaturation during the process is sufficiently slow, the cluster concentrations may have time to assume the steady-state values for the instantaneous temperature and monomer concentration. Raizer[100] deduced a criterion of slowness in the variation of supersaturation for the adiabatic expansion of a cloud condensing in a vacuum.

It can readily be seen that a steady state is attainable only in cases of slow nucleation. Rapid and intermediate types of nucleation are usually accompanied by rapid change in the external conditions. In this case the description of condensation should be based on numerical integration of the set of equations for the concentration variation of critical and subcritical clusters together with the equations for the concentrations of monomer and supercritical species[43]. Methods have been published[16,19] for reducing the number of equations of type (2) to a reasonable level permitting numerical integration on modern computers.

VI. NUCLEATION UNDER NON-ISOTHERMAL CONDITIONS

The theory outlined in Section II describes an isothermal process: i.e. it is based on the hypothesis that the mixture of clusters and monomeric molecules is in contact with a thermostat that will instantly level out local variations in temperature. In real systems the role of such a thermostat can be played only by an uncondensable carrier gas, which dilutes the vapour of the condensable component. Energy is transferred by collisions between carrier-gas molecules and clusters, i.e. at a finite rate. Several non-isothermal effects during condensation arise from the finite rate of energy exchange and the finite number of molecules of the carrier gas[101]: firstly, the mean temperature of clusters of a given size is higher than that of the mixture, with a consequent increased probability of evaporation; secondly, the non-instantaneous removal of the excess of kinetic energy of the condensing molecules may diminish the efficiency of primary acts of addition of molecules to small clusters.

Application of the theory of rate processes to condensation[102] indicates that the transfer of molecules from the vapour to the condensed phase is preceded by formation of an activated complex on the surface. This complex may either dissociate with re-evaporation of the molecule or undergo deactivation, when the molecule will pass into the condensed phase. In the case of a flat surface and sufficiently large clusters deactivation of the complex takes place by the exchange of energy with the condensed phase, the consequent rise in whose temperature is too small to cause immediate vaporisation of another molecule. Deactivation of very tiny clusters can result only from collision with carrier-gas molecules or with molecules of the vapour at the cold end of the energy distribution. In the limiting case of formation of a dimer from two single molecules, a third body must be involved in the collision. Since three-body collisions take place far less often than two-body collisions, the rate of growth of small clusters should be considerably lower than is assumed in the isothermal theory. Furthermore, if nucleation occurs while the temperature of the vapour is falling or immediately after rapid cooling, the temperature relaxation of the clusters will be slower than for free molecules.

Salpeter has recently[103] distinguished three cases of non-isothermal growth of clusters determined by the conditions

(i) $c_p k \gg B/kT$ (large clusters)

(ii) $(B/kT)^2 \gg c_p/k \gg B/kT$ (intermediate clusters)

(iii) $c_p/k \ll B/kT$ (small clusters)

where B is the heat of condensation per molecule, and c_p is the heat capacity of a cluster. By supposing that the temperature of a cluster relaxes exponentially after addition or vaporisation of a molecule, he obtained an expression for the non-isothermal rate of growth of a cluster as a function of a parameter representing the thermal relaxation of clusters and supersaturation. For large clusters a formula for rate of growth was obtained that had been deduced earlier[104]; it predicted that the rate of addition of molecules to clusters during the condensation of water in a Wilson cloud chamber should be much smaller than in the isothermal approximation. The rate of growth found for intermediate clusters from the average temperature of the clusters is zero: i.e. their growth is possible only because of the presence of a temperature distribution both of clusters and of molecules. Salpeter considered that small clusters could grow during

rapid cooling only by the addition not of single molecules but of dimers, from which one of the molecules subsequently vaporised.

As already mentioned in the account of the isothermal theory, its construction on the basis of equilibrium thermodynamics is an approximation, the crudeness of which increases with penetration into the region of metastable states. The use of the Szillard–Farkas model to describe non-isothermal nucleation was until recently not justified at all. However, Bashkirov and Novikov[105], using the non-equilibrium statistical operator method[106], have demonstrated that the notation based on the diffusion of clusters along the size axis can be used also to describe non-isothermal nucleation. In the Reviewers' opinion, nevertheless, this conclusion can relate only to "large" clusters in Salpeter's classification.

The presence of a large excess of a carrier gas relative to the vapour concentration is frequently accepted as the sole criterion of the isothermal character of nucleation. However, the relative departure from isothermal conditions at a constant concentration ratio of carrier gas to vapour n_0/c_1 may vary with I, because the rate of evolution of heat of condensation on nuclei of a given size is proportional not to $\beta_{1g}c_1$ but to the flux $I = f_g(\beta_{1g}c_1 - \alpha_g)$. Thus the isothermal criterion should be

$$\varepsilon = \frac{\beta_{ng}n_0}{\beta_{1g}c_1 - \alpha_g}, \qquad (36)$$

where β_{ng} is the coefficient of collisions between molecules of the inert gas and clusters.

Unfortunately, it is not yet possible to predict by calculation the values of ϵ for which the isothermal approximation could be used, but certain rough estimates may serve as guide. Firstly, the thermal relaxation of polyatomic molecules requires 10^3–10^4 collisions with molecules having the equilibrium energy distribution. On the other hand, Katz[107] made an experimental study of the effect of the quantity of carrier gas on the rate of nucleation in a diffusion cell, and found that I was unaffected if the gas pressure was 50% greater than that of the condensing vapour. Adopting $c_1 \simeq 5 \times 10^{17}$ cm^{-3}, $\beta_{ng} \simeq 10^{-10}$ cm^3 s^{-1}, $I = 1$ cm^{-3} s^{-1}, and Abraham's calculation[97] of $f_g = 10^7$ cm^{-3}, we obtain $\epsilon \simeq 5$. From this last estimate it may be concluded that, with the carrier gas at atmospheric pressure, nucleation is isothermal in character only when $I < 10^2$. It should be noted that Katz was dealing with vapours comprising polyatomic molecules the heat capacity of each of which already exceeded the heat of condensation. In the condensation of monatomic or diatomic molecules the condition $\epsilon \simeq 1$ would be insufficient to ensure isothermal conditions.

Thus the isothermal approximation for nucleation has a very restricted range of application, although it is very often used for comparison with experiment and for engineering calculations under definitely non-isothermal conditions. However, a theory of non-isothermal nucleation has not yet been worked out. Construction of such a theory requires in general consideration of the diffusion of clusters in the size–energy phase plane (which is also approximate, since the possibility of different redistributions of energy between degrees of freedom of the cluster is ignored). Examination of the continuous spectrum of energy states of clusters has not yet been applied, but attempts have been made to replace averaging of the energy state by the division of clusters into two groups, at the equilibrium temperature and activated respectively. Hagena[108] tried to solve a set of differential equations in which the concentrations of activated and relaxed clusters were considered separately, and their interconversion was taken into account. Other workers[109] also discussed two types of states of clusters, but incorrectly neglected the possible evaporation of molecules from thermally relaxed clusters.

On the whole the theory of non-isothermal nucleation still remains in an unsatisfactory state.

VII. EXPERIMENTAL METHODS FOR THE STUDY OF SPONTANEOUS CONDENSATION AND INTERPRETATION OF THE RESULTS

The chief parameters used in the theory of nucleation—rate of nucleation, equilibrium concentrations of nuclei, size of critical nucleus, and free energy of their formation—cannot be measured experimentally. Experiments provide information only on the new phase: its formation when a certain supersaturation is reached is confirmed, the particle size and concentration of the condensed phase are indicated, and in the most favourable case data on the variation in particle size and concentration during condensation are obtained. Such information can be used for comparison, not with the actual theory of nucleation, but only with certain models calculated by use of the theory. Since such models themselves involve various postulates and errors, additional uncertainty is introduced into the problem of agreement between theory and experiment.

The Wilson chamber has been used longest for the study of spontaneous condensation. For decades it has been employed simply to confirm the formation of a disperse phase on attainment of a certain supersaturation, regarded as critical and compared with that predicted by theory. Measurement of the concentration of droplets formed was usually omitted, and the time during which supersaturation was maintained at the critical level was merely estimated. During recent years cloud chambers have been produced enabling a constant temperature to be maintained by means of a programmed expansion cycle lasting tens of times longer than in simple cloud chambers[110,111]. It was found that expansion was adiabatic only in sufficiently large chambers[112]. In view of statements on the possible evolution of foreign condensation nuclei from the walls of the chamber following reaction with atmospheric oxygen[59], experiments began to be made in pure inert gases, and materials for the manufacture of the chambers were chosen more carefully. Reasons were established why the critical supersaturation was lower for repeat expansions: droplets formed in the first cycle had insufficient time to evaporate during the compression period[113].

The most recent work with a Wilson chamber has followed the time variation of the degrees of dispersion and the particle concentration, either by measuring the intensity of scattering of a monochromatic beam of light or by high-speed microcinematography with dark-field illumination. In the former case the mean size is obtained by comparing the measured absolute intensity scattered at a given angle with calculations based on the Mie theory; measurement of the angular dependence of the polarisation ratio of light scattered by the particles will give the width of their size distribution[114–116].

Comparison of theory with experiment at only the one, critical supersaturation, although giving less information, is logically more soundly based, since it describes more correctly the metastable state of the vapour, not the

breakdown of this state. However, the need to establish methods of calculation for engineering bulk condensation compels the use of nucleation theory even to describe processes in which nucleation takes place on a background of exhaustion of the vapour. Allowance for the decrease in supersaturation due to consumption of the vapour was first proposed by Tunitskii[117]. A more accurate method, requiring simultaneous numerical integration of the equations of adiabatic expansion, nucleation, and condensation growth of particles, was suggested by Courtney[118] and then used in many papers for the interpretation of experimental results,

A method for the study of bulk condensation—the diffusion cell—has recently been used very successfully by Katz[120,121] following its early first application[119]. Gradients of temperature and vapour concentration are established between two plates (by evaporating the vapour from the hot plate and condensing it on the cold plate). Because of the non-linear temperature dependence of the vapour pressure the vapour becomes supersaturated at some distance from the hot plate, and the supersaturation may exceed the critical value. Formation of the condensed phase can then be detected by the usual methods. In contrast to the Wilson chamber, condensation here is a steady-state process, which is a great advantage. Furthermore, the diffusion cell is self-purifying: i.e. various impurity centres of condensation are immediately removed by the condensing vapour. In this case comparison of theory with experiment reduces to calculating the height distribution of supersaturation, determining the level at which mist is formed, and thus finding the critical supersaturation.

Just as in the Wilson chamber, supersaturation by adiabatic cooling is produced during supersonic flows of vapour and vapour–gas mixtures through a nozzle. Investigations of condensation under such conditions have become widespread because of the great interest for energetics presented by the possibility of controlling formation of the disperse phase. Condensation is studied by measuring the static pressure distribution along the axis of the nozzle (formation of a condensed phase is accompanied by a change in pressure), by observing the flow with shadow optical instruments (schlieren) and by measuring the scattering of a laser beam in different cross-sections of the nozzle. The last method will now detect the formation of particles of mean size 20 Å.[115] Many studies have now established agreement between the mass of the condensed phase calculated from changes in the static pressure and from light scattering[114,122]. Results of the determination of the mass of the condensed phase or of the mean size of the particles and their concentration are compared with those of the simultaneous numerical solution of the equations of the conservation of mass, energy, and momentum, the equation of state, and the equations for the number of particles

$$\mathrm{d}n_g/\mathrm{d}t = I(t) \qquad (37)$$

and for particle growth by condensation. Such a set of equations was first used and solved analytically with several simplifications by Oswatitsch[123]. More accurate methods requiring numerical integration have been described by several authors[124–126]. Especially noteworthy is the work of Campbell and Baktar[124], whose methods of calculation yield not only the mean particle radius but also the size distribution, since separate kinetic equations are written for the growth of particles formed in different portions of the flow. In the Reviewer's opinion, however, these authors made several unnecessary postulates (e.g. neglect of the growth of nuclei beyond the critical size in the zone where they had been formed). In calculations on condensation most authors use free molecular rotations in the kinetics of the growth of particles and the transfer of heat to them, which is incorrect, since with particle growth the Knudsen numbers characterising the régime of heat and mass transfer to the particle become too small for free molecular rotations to remain applicable. However, the main complexity in the use of nucleation theory for such calculations is the great non-uniformity and non-isothermality of the process when the vapour escapes in the absence of a carrier gas.

Adiabatic cooling of a gas takes place also in so called high-intensity molecular beams, which are fine, supersonic jets emerging into a high vacuum, from which the central portion of the flow is isolated by means of a set of conical diaphragms[127]. Very rapid and strong cooling is achieved in such flows. Formation of molecular aggregates comprising tens, and sometimes even thousands, of molecules can be detected by means of ionisation detectors, as well as by time-of-flight and quadrupole mass spectrometers. Information on the size of clusters formed in molecular beams can be obtained from measurements on its weakening by a cross beam. Measurement of the weakening of the latter beam will also give the fraction of monomer uncondensed. Such a method was used to study the agglomeration of clusters after complete exhaustion of the monomer[128], i.e. essentially coagulation in the beam.

The state of the internal degrees of freedom of molecules in such beams is very far from equilibrium: their vibrational, rotational, and translation temperatures may differ several-fold. Thus the formation of clusters of polyatomic molecules in such beams has little in common with the concepts of nucleation theory. The main use of such experiments is to provide information on the primary acts in the aggregation of monatomic molecules and on the possibility of the formation of mixed molecules aggregates by the condensation of multicomponent systems. The interpretation of data obtained by means of powerful molecular beams is complicated by the inability of existing escape theories to explain certain qualitative features—e.g. the presence of maximum intensity at a certain distance along the beam between the nozzle and the first conical shield (skimmer)[129,130] and the angular separation of components differing in mass.

Cooling during the molecular diffusion of a vapour through a cold gas takes place in certain forms of equipment for the production of metal powders. Such experiments give some useful information on the condensation of metal vapours. Similar results are obtained in experiments on exploding wires, in which cooling is due both to the diffusion mixing of the vapour with the surrounding gas[76,131].

Several studies have been made on condensation during the turbulent mixing of a hot vapour–gas mixture and a cold gas. The Reviewers have shown[132] that calculation of condensation in turbulent flows must take into account the three-dimensional transport of clusters by the turbulent vortices, so that Eqns. (2) for the description of nucleation must be replaced by the set of partial differential equations

$$v\,\mathrm{grad}\,f_g = \mathrm{div}\,(D_t\,\mathrm{grad}\,f_g) + I_g, \qquad (38)$$

where v is the time-average rate of flow, I_g the operator of the right-hand side of Eqn. (2), and D_t the coefficient of turbulent diffusion.

Another peculiarity of the condensation consists in the effect of turbulent pulsations of temperature and concentration. Pulsations lasting longer than the relaxation time of deviation may obviously distort significantly the course of condensation, but this aspect has not yet been investigated. In spite of these complicating factors, it is necessary to investigate condensation in turbulent flows, because such processes are often met in technology. Furthermore, turbulent mixing is convenient for the study of condensation at high temperatures. The above complications disappear when mixing precedes condensation, i.e. with rapid mixing and slow condensation—and hence at low vapour concentrations—even if condensation may be of the "rapid" type.

A one-dimensional approximation was suggested[13,14,16] for calculating condensation in a submerged turbulent jet. This involves numerical integration of an equation, averaged over time and angle, for rate of mixing and a set of equations (2) for the concentrations of small clusters, as well as equations for the growth of supercriticalt particles of average mass. In another modification of this method, applicable to processes in which coagulation predominates, Eqns. (2) are combined with the coagulation equations of the Rosinski–Snow model[133]. Amelin et al.[134] suggested a method for studying condensation during turbulent mixing, in which nucleation and enlargement of the particles took place in different apparatus, so that there was no need to consider exhaustion of the vapour during nucleation. Equipment in which a vapour–gas mixture is diluted by a coaxial flow of a cold gas in a diffuser with cooled walls has been used[135] to study condensation in a turbulent flow; these experiments were interpreted on the assumption that condensation is preceded by mixing.

Shock tubes have also been used for the study of nucleation. They may serve two purposes: in some cases[136] vapour condensers in the rarefaction formed behind the detonation front; in other cases the heating effect of the detonation wave causes decomposition of a chemical compound with formation of a non-volatile component, whose condensation is studied[137].

VIII. EXPERIMENTAL RESULTS ON SPONTANEOUS CONDENSATION

The large majority of experimental results, including those on the condensation of one-component systems, compare with the predictions of the isothermal theory, although isothermal conditions are not always observed even when condensation is studied in the presence of a carrier gas. In Wilson chambers possible non-isothermal effects become more intense with rise in the initial temperature.

Calculations based on the classic theory[118,141] agree with results on the condensation of water[110-112,138-140] only within a narrow range of supersaturations. On the whole the experimental dependence of rate of nucleation on supersaturation has a smaller slope than the theoretical curve, and intersects the latter at $S = 5$. Observations on the establishment of a steady state in Wilson chambers indicate a slower increase in I than is predicted by Courtney's calculations[118] or else agree with them only at low temperatures[138]. We recall that these calculations[118] use a formula for I which is smaller by the factor $1/S$ than that obtained by Frenkel'. The slower experimental attainment of a steady state may indicate either that the condensation coefficient is lower with small nuclei or that the process is non-isothermal.

Special attention should be given to the extremely thorough and carefully conducted work by Kassner and his coworkers[110,111,140], in which the rate of nucleation was measured as a function of supersaturation for several temperatures by the use of various inert carrier gases. These results are fully consistent with those obtained earlier, and support all the earlier conclusions, but cover far wider ranges of temperature and supersaturation. Among the important conclusions reached by these workers was that, when the supersaturation is maintained constant after expansion, the rate of formation of new particles does not remain constant, but diminishes, the effect becoming more marked with increase in supersaturation. This phenomenon was explained by the presence in water vapour of molecular nuclei, whose concentration is proportional to that of the vapour. The I–S curve has a point of inflexion in the range $I = 10$–100 cm^3, which is most clearly defined at low temperatures. The experimental curve generally intersects the curve calculated on the classic theory, so that the rate of nucleation is underestimated at low supersaturations, and overestimated at high supersaturations. On the other hand too high rates at low supersaturations are explained by the substantial contribution of heterogeneous condensation on molecular condensation nuclei. Rates are distinctly greater in heavy than in light inert carrier gases.

Allard and Kassner[110] attributed the formation of foreign nuclei to the radiolysis of water vapour by the background cosmic radiation. The heterogeneous character of condensation at low supersaturations most probably applies to all other experiments on the condensation of water in Wilson chambers. The difference between results obtained in argon and in helium was explained on the hypothesis that these gases form clathrate compounds with water, of which the argon clathrates are the more stable. The untenability of this hypothesis was shown by Burke[142], who also suggested possible mechanisms of the radiation formation of foreign nuclei and pointed out that argon, which should act as a third body in several of the reactions involved, will ensure a greater cross-section of three-body reactions than will helium, which explains the difference in the kinetics of condensation in these gases. Moreover, argon promotes more rapid removal of heat from nuclei than occurs with helium, as follows from Luke's calculations[143]. Clark and Noxon[144] reported the formation, under the influence of ionising radiation in helium containing unsaturated water vapour, of particles reaching 10^{-4} cm. This also supports the heterogeneous character of condensation at low supersaturations. The formation of aggregates $Ar_x(H_2O)_y$ was reported[145], but at far lower temperatures than in the experiments of Allard and Kassner.

The point of inflexion on the I–S curve was explained by White and Kassner[146] on the hypothesis that an electrical double layer is formed on the surface of aqueous clusters by the orientation of water-molecule dipoles. Such a point was indeed present on the dependence of rate of nucleation on supersaturation which they obtained by using a formula for ΔG allowing for the contribution by a double layer, but this contribution was only estimated.

The temperature dependence of the critical supersaturation was studied on methanol, ethanol, water, hexane, octane, nonane, and heptane by Katz and Ostermeyer[120] and by Katz[121]. The hot plate, from which vaporisation

occurred, was located at the bottom of the diffusion cell used, so that, to avoid mixing by convection currents, the temperature gradient had to be balanced by a composition gradient in the vapour–gas mixture, with a light gas (hydrogen, helium, or neon) at reduced pressure employed as carrier. As a consequence, the concentration ratio of vapour and carrier gas was still lower than is usual in Wilson chambers, which is dangerous to isothermal conditions. However, this aspect might be unimportant, since most experiments were made with polyatomic substances, for which the difference in heat capacity between condensed and vapour phases is relatively small. For organic compounds these workers obtained very good agreement with the classic theory in the Becker–Döring form; for water, however, as in Wilson chambers, agreement was observed only over a narrow temperature range and with considerable scatter.

Reiss and Heist made accurate measurements of the critical supersaturation of water vapour in a diffusion cell over a wide temperature range[147]. Their results show little experimental scatter and give S_{cr} values 8% above those predicted by the Frenkel' formula. In contrast to measurements in a Wilson chamber, the nature of the carrier gas is of no significance in a diffusion cell. This indicates truly isothermal conditions and the absence of foreign nuclei, whose formation involves molecules of the inert gas.

Formation of a condensed phase during supersonic flows of a one-component vapour, of course, cannot be described on the basis of the isothermal theory. It is not surprising, therefore, that the large majority of results for the condensation of water vapour in nozzles can be reconciled with calculations based on the classic theory only after the introduction of empirical parameters. A single parameter, e.g. a condensation coefficient less than unity, is insufficient to obtain the correct form of static pressure curve. Therefore two or three parameters are generally employed[124,148–151].

Non-isothermal conditions are not in general the sole factor casting doubt on the use of steady-state solutions of the classic theory to describe condensation in nozzles. The large supersaturations and the small critical nuclei indicate that the processes occurring in nozzles belong to the rapid type of nucleation. Introduction of a correction for the non-stationary character of the process in these cases is equivalent to adjusting the condensation coefficient, and by itself, therefore, cannot improve the agreement with calculations.

In contrast to the above results the later papers by Wegener and his coworkers[114,152] on the condensation of water vapour gave good agreement with the classic theory for liquid nuclei with $\gamma = 0.01$. In his earlier papers Wegener[153,154] had obtained agreement only by adopting lower values for γ and postulating that the nuclei had a crystalline structure.

A group of investigators[155,156] studied the condensation of the vapours of water, benzene, chloroform, and trichlorofluoromethane at partial pressures of 0.01–0.1 mm in air emerging through a Laval nozzle. At low supersaturations the rate of condensation of water was predicted satisfactorily on the basis of the classic theory with $\gamma = 0.01$, but the organic liquids condensed significantly more rapidly than might have been expected from calculations with $\gamma = 1$. These results may be affected by the presence of impurities, most likely water. The same workers found[156] that 0.001% of water greatly accelerates the condensation of ammonia, which is explained by the greater rapidity of binary nucleation.

Great interest attaches to the non-stationary jumps in condensation occurring in Laval nozzles, a phenomenon studied in detail by Deich et al.[157] and given a theoretical explanation[158,159]. The jump in density preceding the jump in condensation moves upstream into the subsonic zone, as a consequence of which the jump in condensation moves downstream, until the effect of the former jump on the flow parameters becomes negligible and jumps reappear at the previous sites. The frequency of the oscillations in the position of the condensation jump reaches 1 kHz. This phenomenon illustrates clearly the non-isothermal character of condensation in nozzles. A peculiar type of condensation with adiabatic cooling was predicted by Deich and Filippov[159] and investigated experimentally by Deich et al.[160]; it involved condensation by turbulent perturbation of a subsonic unary flow, in which the supersaturation was considerably less than the critical value.

A considerable number of studies with Laval nozzles were made on condensation in the presence of two condensable components. However, the thermodynamic properties of the components frequently differed so greatly that the start of condensation of the more volatile component was preceded by formation of large drops of the less volatile component. Hence the results relate to heterogeneous condensation rather than to homogeneous binary nucleation. The condensation of mercury is accelerated by the introduction of rubidium vapour and of nitrogen, as well as on the addition of argon[161]. The need to use higher values of σ to bring calculation into agreement with experiment gave rise to hypotheses[42–66] as to the structure of aqueous clusters, which should actually have possessed a surface tension greater than σ_0. In the Reviewers' opinion the divergence of theory from experiment has other explanations—non-isothermal and non-equilibrium conditions, decrease in γ with small nuclei, non-monotonic dependence of the free energy of formation of nuclei on their size.

Experiments[134] on the condensation of water vapour with turbulent mixing of flows at the same temperature gave a result analogous to those obtained by other methods: the rate of nucleation exceeds the theoretical value at low supersaturations, but is smaller at high separations. The same situation has been observed for the vapour of dibutyl phthalate.

Study of the rapid type of nucleation is still more complicated than that of the slow type, since in this case a relatively short period of nucleation is followed by coagulation, which begins when even the coarsest particles of the condensed phase do not exceed 100 molecules[13]. Because coagulating systems tend to "forget" their initial state, it is difficult to reach any quantitative conclusions on the process of nucleation. In such a case the only requirement of theory is a reasonable estimate of the lag in the early stages of the agglomeration of vapour molecules relative to systems in which avalanche condensation takes place with 100% collision efficiency.

Some idea of the character of rapid nucleation could be obtained from studies on the condensation of very dilute inorganic vapours and the mechanism of the formation of highly disperse uncoagulated aerosols[162–164]. It is well known that such aerosols of low number concentrations can be obtained when a gas flow passes over the heated surfaces of metals, their oxides, and their salts. Calculation shows that the critical nucleus is very small in such cases, most probably a dimer, whose condensation provides a typical example of the second type of nucleation. The aerosol obtained would be of coagulation origin: i.e. with short lifetimes of the condensing system the number

concentration is high and the scatter of sizes large. The experimental observation of relatively monodisperse aerosols of low number concentration can be explained only by the heterogeneous origin of the particles. The problem remains as to why homogeneously formed particles are not observed in these experiments. The only possible explanation is the dependence of the efficiency of collisions of vapour molecules with clusters on the size of the latter, which has been discussed in Section IV. Computer experiments simulating agglomeration of a vapour involving such a dependence showed that the induction period in the formation of homogeneous particles may be sufficiently long for the vapour to condense on the walls before the appearance of particles formed by homogeneous condensation. Since the length of the induction period decreases with increase in the initial vapour concentration, it may be expected in some cases that particles may, nevertheless, be formed by condensation, but they will be significantly smaller than those resulting from heterogeneous condensation on impurity nuclei.

This prediction has been confirmed experimentally[16,163] for the vapours of silver, sodium chloride, and silver iodide. It is interesting that the difference in size between particles formed homogeneously and heterogeneously was quite large in the agglomeration both of monatomic and of diatomic molecules: i.e. formation of a dimer of a diatomic molecule also requires the participation of a third body. The possible dissipation of excess kinetic energy in an internal degree of freedom of the diatomic molecule is evidently insignificant.

The fact that formation and growth of the smallest clusters are possible only as a consequence of three-body collisions will explain the dependence of particle dispersion on experimental conditions. The decrease in particle size as the gas pressure falls in the diffusion of metal vapours through rarefied inert gases[16,131,165] can be attributed to the increasing rarity of three-body collisions and the attainment of the earlier stages of agglomeration. The increase in dispersity when argon is replaced by helium is explained similarly: the latter is less efficient as a third body, which also slows down agglomeration. The fact that from a certain point further decrease in gas pressure has no effect can be attributed to the coalescence of fine particles after their deposition on the walls.

Considerable understanding of the course of the early stages in the aggregation of molecules has been provided by experiments on high-intensity molecular beams. Miln et al.[166] compared the results of computer experiments simulating the kinetics of dimerisation in a fine supersonic jet of argon with the measured concentrations of dimers, and found that at sufficiently low temperatures the termolecular rate constant is similar in order of magnitude to that calculated for the three-body collision cross-section of solid spheres. However, the strong temperature dependence of the constant suggests that not all three-body collisions result in formation of the dimer. The dissociation constant of the dimers was estimated in this work by the method of Stogrin and Hirschfelder[90]. Golomb et al.[167] found $k_3 = 3 \times 10^{-33} T^{1/2}$ for the termolecular dimerisation constant of argon; the concentrations of dimers were 25–50% of the equilibrium values calculated according to Stogrin and Hirschfelder.

Concentrations of dimeric argon closely similar to those calculated by this method were observed by Milne[168]. The addition of nitrogen and argon to a jet of carbon dioxide has the opposite effect on the kinetics of the formation of clusters. His explanation was that the drop in temperature of the escape of nitrogen into a vacuum is slower than with argon, so that dimers of the latter are more effective as third bodies in the collisions of carbon dioxide molecules. The rate of formation of dimers in an argon beam was greatly diminished by additions of polyatomic molecules. Mixed clusters Ar_xH_2O and $Ar(H_2O)_x$ were detected. Henkes[169] established by mass-spectrometric analysis of products from the condensation of carbon vapour that the concentrations of clusters decrease non-monotonically with increase in their size. This can probably be attributed to a non-monotonic variation in the free energy of formation of clusters with their size.

Hagena and Obert[170] found that similarity was observed in the condensation of neon, argon, xenon, krypton, nitrogen, and carbon dioxide in a supersonic jet. In particular, mean cluster size remains constant with variation in the pressure preceding the nozzle, provided that the temperature in the nozzle varies simultaneously to maintain $p_0 T_0^{\gamma/(\gamma-1)}$ constant (where γ is the exponent of the adiabatic curve). Similarly, the particle size of the condensed phase remains constant with variation in nozzle diameter if $p_0 d^q$ remains constant, where q has the values 0.8 and 0.6 for argon and carbon dioxide respectively. Dimerisation in molecular beams of carbon dioxide takes place[171] only as a result of three-body collisions. The dependence of the concentrations of large clusters (beginning with the trimer) on the pressure in the source and the diameter of the nozzle shows that they may be formed by the combination of single molecules with smaller clusters without the involvement of third bodies. The efficiency of collisions of the monomer with $(CO_2)_x$, where $x = 2$–4, is ~0.03.[172]

It is interesting that Hill and Whitfield[173] observed chemiluminescence in the condensation of nitric oxide, which they attributed to oxidation of a molecule in a cluster to nitrogen dioxide and its detachment in an excited state followed by emission of a photon. The yield of photons is 20% of the number of $(NO)_x + O_2$ collisions. In the Reviewers' opinion this phenomenon indicates that the excitation of an individual molecule in a cluster does not lead to breakdown of the latter; it is of interest in connection with the possible disintegration of clusters on ionisation in the sources of the mass spectrometers normally used for the emission of molecular beams. Becker et al.[174] studied the reflection of nitrogen clusters from a stainless-steel surface. Dissociation of the clusters was not observed on reflection, and the intensity of the beam was almost independent of the temperature of the surface: i.e. the clusters did not absorb energy during the collisions. The beam had greatly narrowed on reflection, since the velocity of the clusters remained constant only parallel to the steel surface. The angles of incidence of the clusters lay in the range 50–75°, and the angles of reflection between 85° and 90° to the normal to the surface. These observations throw a somewhat unexpected light on the character of energy transfer in clusters.

From a study of the formation of a lead aerosol by the decomposition of tetramethyl-lead vapour in a shock tube at 920–960 K Graham and Homer[137] concluded that coagulation is the main factor determining the course of the particle-size distribution in this case. They were able to measure the aerosol coagulation constants, and showed that the decrease in particle concentration with time obeys a $t^{-6/5}$ law, which indicates establishment of a self-sustaining régime of coagulation.

Barschdorf[175] studied the condensation of water vapour in a shock tube in the presence of various carrier gases. He found that, with a mass fraction of the vapour of 0.1,

the classic theory underestimates the rate of nucleation, depending on the nature of the carrier gas, by factors of 30–1000. At higher moisture contents the rate of smaller than the calculated value, and for the pure vapour theory overestimates I by factors of 10–100. The condensation of the vapours of chloroform and Freons in a shock tube was far more rapid than according to the classic theory.

Isothermal condensation of the vapours of several compounds—alcohols, n-alkanes, esters, and a number of acids—is well described by the classic theory based on the usual surface tension. The rate of nucleation is underestimated, but the discrepancy between theory and experiment can be eliminated by using values of the surface tension found by Band's method[36] from the equation of state of the vapour. For water, sulphuric acid, and certain other compounds theory predicts too low a rate of nucleation at low supersaturations, and too high a value at high supersaturations; no satisfactory explanation has yet been given for this divergence. Nevertheless, the condensation of water has been studied over a wide range of conditions, including non-isothermal conditions with water vapour escaping through a nozzle under various régimes. This permits the use for engineering calculations of formal expressions for the rate of nucleation with empirical corrections.

In the case of the rapid type of nucleation, with a sufficiently long lifetime of the condensing system $t > \theta^* \gg \theta$, the degree of dispersion and the concentration of the condensed phase can readily be calculated by means of known solutions of the coagulation equations, without the need to determine the bonding energy of small clusters or to obtain detailed information on the primary acts of condensation. Results obtained by several workers on these lines permit θ^* and θ to be estimated, and also indicate that θ^* never exceeds $\sim 10^4$. When $t < \theta^*$, the description of rapid condensation requires the above information, which has been successfully accumulated in work using molecular beams.

The theory of non-isothermal nucleation remains in an unsatisfactory position. Most real cases of condensation take place in multicomponent systems. Metastable states of such systems have been subjected to only most general examination[32]. No practical advances in the description of nucleation in multicomponent systems have been made since the early work of Reiss[176,177]. Some little experimental investigation has been made on nucleation in binary mixtures, but not at all in multicomponent systems. It is extremely desirable to develop experimental methods for direct examination of the properties of small clusters and of primary acts in condensation. The only technique used for the latter purpose—molecular beams of high intensity—deals with molecules whose state is far from equilibrium.

Great difficulties are presented by the study of chemical condensation, in which disperse particles arise from chemical reaction in the gas phase. For the present, qualitative and semi-quantitative data are being accumulated on the role of various factors in these complicated processes. The greatest progress has been made in connection with the formation of carbon black[178] and also of photochemical smog[179]. Sufficient attention has not yet been paid to the theoretical study of chemical condensation in other systems, especially in simplified model cases.

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