GENERAL DISCUSSION

Dr. E. R. Buckle (*University of Sheffield*) said: In introducing his paper Dunning compared the experimental nucleation rates J_{exp} for water condensation with those predicted by the so-called " classical " theory, J_{theor}, such that by and large $J_{exp}/J_{theor} \sim 10^3$. What confidence can be placed on the actual values given for J_{exp} by the various workers?

Dr. W. J. Dunning (*Bristol University*) said: Prof. J. Clumpner (now at the American University, Beirut) has considered all the possible errors (including the so-called " influence coefficients " of gas dynamics) which may affect the evaluation of J_{exp} from the Yale nozzle experiments. His conclusions have not yet been published, but I understand that for the best work, J_{exp} is known to within a factor of 10 and there is no problem in achieving a factor of 10^2. Clearly the precision is adequate to discriminate between theories which predict values of J which differ by factors of 10^{12}-10^{17}.

Dr. C. S. Kiang (*Clark College, Atlanta, Ga.*) said : Would Dunning comment on the present state of his eqn (6)?

Dr. W. J. Dunning (*Bristol University*) said: In reply to Kiang's question of the present status of my eqn (6), experimenters find it useful to compare their results with classical theory (my eqn (6)) by using a factor Γ_{exp} to match this theory with their experimental results

$$J_{exp} = \Gamma_{exp} \cdot J_{class}.$$

In the same way, it is useful to compare the rates of nucleation J_{theor} predicted by the different theories

$$J_{theor} = \Gamma_{theor} \cdot J_{class}.$$

For example, Lothe and Pound's [1] theory predicts $\Gamma_{L-P} \sim 10^{17}$, and my theory [2] predicts $\Gamma_D \sim 10^4$ for water vapour condensation.

The careful work of Wegener, Clumpner and Wu [3] on the nucleation and growth of ethanol drops in supersonic flow yielded values of Γ_{exp} at different stations x along the nozzle (fig. 1). Also illustrated in the figure are the corresponding values of Γ_{LP} and Γ_D ; if the classical theory applied, Γ_{exp} would run along the x axis. The value of Γ_{LP} at the onset point is about 10^{17}, the value of Γ_D at this point is about 10^5, matching the experimental value of Γ_{exp} closely. Thus, the Lothe–Pound theory predicts nucleation rates which are far too high ; classical theory predicts rates which are rather low (10^{-5}). In these ethanol experiments the following conditions are favourable. The ethanol was carefully purified, the mass-fraction of water vapour in the air was less than 10^{-6}. The critical nuclei are comparitively large, containing 15-20 molecules. The condensation takes place above the triple point so that the nuclei are almost certain to be liquid.

In the presence of a carrier gas (e.g., air), the nuclei and droplets grow under

[1] Lothe and Pound, *J. Chem. Phys.*, 1962, **36**, 2080.
[2] Dunning, *Adsorption et Croissance Cristalline* (Coll. Int. C.N.R.S. no. 152, Paris), 1965.
[3] Wegener, Clumpner and Wu, *Phys. Fluids*, 1972, **15**, 1869.

isothermal conditions; for pure vapour (e.g., steam) the nuclei and droplets are at a higher temperature than the vapour and nucleation proceeds more slowly. In fig. 2,* the values, uniformly calculated, of Γ_{exp} for ethanol, water and benzene are shown plotted against the mass-fraction ω_0 of vapour. For the two latter substances, there is more uncertainty about the thermodynamic state of the nuclei and the results for both solid and liquid states are shown; in each case the lower of the pairs is to be preferred for kinetic reasons. Barschdorff, Dunning, Wu and Wegener have recalculated all experimental results for pure steam and these are all in the range of the hatching at log $\omega_0 = 0$. These results give $10^{-2} < \Gamma_{exp} < 10^6$ to be compared with $\Gamma = 1$ if the classical theory held, and with $\Gamma_{LP} \sim 10^{17}$ and $\Gamma_D \sim 10^4$.

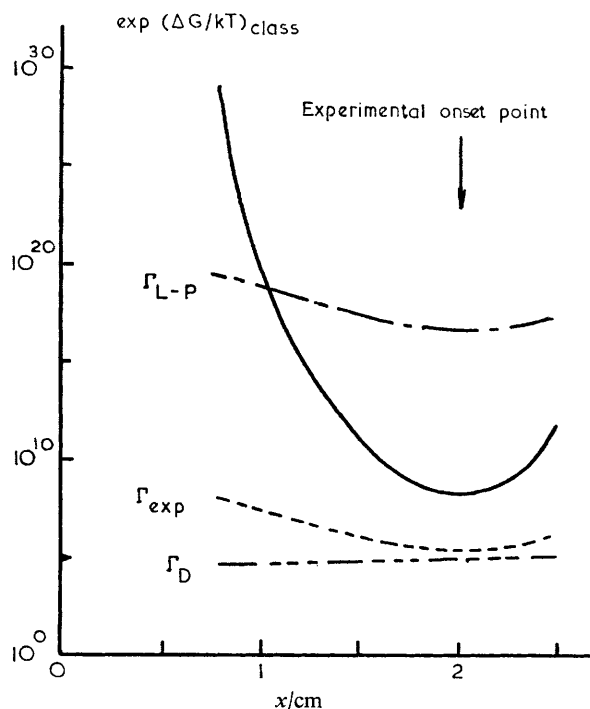FIG. 1.—Nucleation of ethanol in air. Showing the dependence of Γ_{exp}, Γ_{LP}, Γ_D on x, the station, after Wegener, Clumpner and Wu, ref. (3)).

Using a shock tube, Barschdorff * (unpublished) has investigated the effect of various carrier gases at various mass-fractions on the nucleation rate for water vapour and his results are illustrated in fig. 3; here, $J_{exp}/J_{theor} \equiv \Gamma_{exp}$ is plotted against ω_0 and we find $10^{-2} < \Gamma_{exp} < 10^3$. Investigations on other materials have not been so intensive. Pure nitrogen gives $\Gamma_{exp} \sim 10^{-6}$. On the other hand, experiments on freon and chloroform have given results close to values predicted by the Lothe–Pound theory.

4 Dawson, Wilson, Hill and Russell, *J. Chem. Phys.*, 1969, **51**, 5389.

GENERAL DISCUSSION

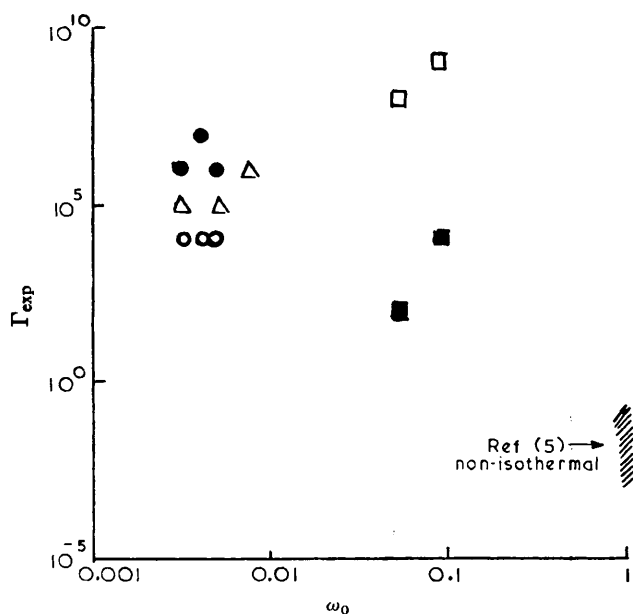Fig. 2.—Nucleation of ethanol, water and benzene. Γ_{exp} as a function of the mass-fraction ω_0 of the substance in air (courtesy of Prof. P. Wegener). $\triangle$, Ethanol; $\bigcirc$, $\bullet$, H_2O; $\square$, $\blacksquare$, benzene; open symbols, liquid; solid symbols, crystal.
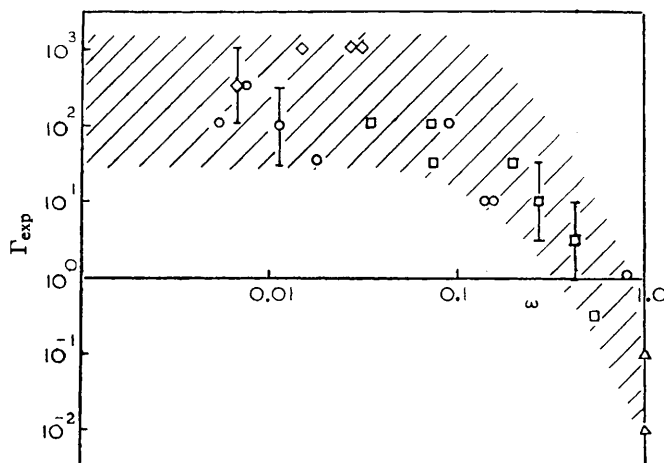

Fig. 3.—Nucleation of H_2O. Γ_{exp} as a function of ω_0 for various carrier gases. $\triangle$, Steam; $\bigcirc$, H_2O in argon; $\square$, H_2O in helium; $\diamondsuit$, moist air.

It must be remembered that " binary " and " hetero-molecular " nucleation theory as discussed by Kiang and Stauffer in this Discussion, indicates that impurities in the substance examined would, if they were effective always tend to increase the value of Γ_{exp}.

Prof. M. Kerker (*Clarkson Coll. Techn., Potsdam*) said: I would ask Dunning, what can be said about the form of the size distribution prior to the onset of coagula-

tion? We have assumed that the aerosols, having a somewhat narrow size distribution, formed by condensation upon heterogeneous nuclei, could be represented by a logarithmic distribution.

Dr. W. J. Dunning (*Bristol University*) said: In reply to Kerker, the mathematical form of the classical nucleation rate equation seems to be accepted, although the values of some of the parameters have been subject to controversy. In a well-defined experiment, it is possible to calculate the rates of nucleation and the rates of growth and evaporation of all classes of particles at all stages of the collapse of the supersaturation. Thus the form of the size distribution is ascertainable under such conditions. It is necessary to check by calculation the progress of coagulation since, under certain circumstances, coagulation may become significant before growth is effectively complete.

I have no experience of the Kerker type of aerosol generator and I cannot judge how well defined the thermodynamic variables are. It may be possible to idealize it and calculate the aerosol size distribution to be expected. In this, one could assume that, Volmer's theory of heterogeneous nucleation was valid and that an appropriate rate of growth was applicable and at least determine the form of the size distribution thus predicted. Until such studies are made, it is not possible to assess whether the logarithmic distribution closely approximates the experimental distribution or not.

Dr. E. R. Buckle (*Sheffield University*) (*communicated*): The size distribution in a spontaneously condensed aerosol will adjust by growth and evaporation towards the stationary form of eqn (1.3) of my paper, which resembles Volmer's distribution (eqn (1.18)). If the conditions change, the system will approach a new distribution of similar form. The distribution will be cut off at a size in the region of the critical size in the early stages but eventually will extend to larger sizes as the result of coagulation. In seeded condensation it may happen that the growing centres are too large at the outset for them to qualify as labile gaseous species, and the distributions of my paper would not apply.

Prof. C. S. Kiang and **Dr. D. Stauffer** (*Clark College, Atlanta, Ga.*) said: Would Dunning give his opinion of the reason why some materials obey classical nucleation theory and some do not. Theoretically, the capillarity approximation using the bulk surface tension for small droplets may be inaccurate. Computer simulations of small droplets (" micro-crystalline calculations ") do not need such an approximation. Calculations of this type by Burton [1] explain from *one* model most of the observed deviations from and agreements with the classical nucleation theory. His comparison with classical theory depends on the temperature and the supersaturation, which are different for different experiments. (In another preprint, Burton proves convincingly the presence of a Lothe–Pound translation–rotation term in such microcrystalline calculations based on vibration frequencies and binding energies of the molecules. This does not yet solve the question whether the capillarity approximation requires, too, a Lothe–Pound correction since it might already be included in the effective surface tension.)

Another (simpler but so far less successful) approach is to make the capillarity approximation, to neglect the Lothe–Pound factor, but to use a microscopic droplet surface tension different from the measured bulk surface tension. The smaller the

[1] J. J. Burton, *Acta Met.*, to be published.

droplet surface tension is compared to the measured bulk surface tension, the higher should the nucleation rate be compared with classical theory. We determined this " microscopic " surface tension from the two methods,[1] (density)/(critical density) and from 1-PV/RT. We found, for H_2O, CH_3OH, and C_2H_5OH, good agreement of these microscopic surface tensions with the bulk surface tension. (Experimentally, classical nucleation theory works here.) For NH_3, C_6H_6, $CHCl_3$, and $CFCl_3$, the microscopic surface tensions were much lower than the bulk surface tension (classical nucleation rates are too low here). But unfortunately, for hexane, heptane, octane, we also found lower microscopic surface tensions although classical theory works here.

Experimentally, the possibility cannot be excluded that the water impurities in NH_3 lowered the supersaturation necessary for nucleation.[2] Our paper on hetero-molecular nucleation indicates that such effects are quite strong for $H_2O + H_2SO_4$.

Dr. W. J. Dunning (*Bristol University*) said: In reply to the question of Kiang and Stauffer, all possibilities should be considered.

With regard to Stauffer's report on calculations by Burton, if we imagine a bulk crystal containing $n = km$ particles to be subdivided into m crystalline nuclei each containing k particles and if ε_k° is the specific surface energy and O_k the surface area of a nucleus, the replacement factor q_{rep} will be [3]

$$q_{rep} = (\varepsilon_k^\circ - \sigma_\infty)O_k + \sum_{j=1}^{3k-6} (\phi_j + \eta_j) - \frac{1}{m} \sum_{i=1}^{3n-6} (f_i + \varepsilon_i).$$

In this, σ_∞ is the surface tension of the bulk crystal, ε_i and η_i are the zero-point energies of the ith and jth normal modes of vibration in the nucleus and in the bulk crystal respectively, and f_i and ϕ_j are their free energies, given by

$$\phi_j = -kT \log \sum_{n_i \geqslant 0} \exp(-hu_j n_j/kT)$$

with a similar expression for f_i.

The calculation of q_{rep} thus requires a precise evaluation of ε_k° and the frequencies μ_j of the normal modes in the nucleus and in the bulk crystal.

Dr. E. R. Buckle (*University of Sheffield*) said: The contention in the original paper of Lothe and Pound (ref. (20) of Dunning's paper) was that the Volmer theory of nucleation is in error in taking no account of the natural chaotic motion of the growing nuclei in the parent phase. I know of no reason for supposing that it was in Volmer's mind that the embryonic particles were motionless, so that it is to be presumed that the particle distribution in his treatment (eqn (1.18) of my paper) was intended to be one of equilibrium involving all thermally accessible energy levels in the various degrees of freedom.

In the kinetic formulation of the problem given in ref. (1) of my paper, the terms W_g' and W_g'' of Volmer's theory are given their molecular interpretations for vapour condensation. The collision terms for the motion of the gaseous clusters appear in the quantity ζ_g, the interfacial free enthalpy. As stated in my paper, $\zeta_g = W_g'$, so that the same terms are contained in γO_g of Volmer's formula. The Brownian motion is therefore taken into the surface tension term, and the error in Volmer's formulation of the reversible work of nucleus formation will reside in the use of a single value of

[1] *J. Atm. Sci.*, 1972, **28**, 1222: Appendix B.
[2] see *J. Chem. Phys.*, 1972, **51**, 5380, in particular, p. 5387.
[3] W. J. Dunning in *Nucleation*, ed. A. C. Zettlemoyer (Marcel Dekker, New York, 1969), p. 35.

surface tension for all cluster sizes. As a likely source of error, this has long been appreciated, and the conclusion is that there is no additional source of error due to the omission of thermal motion terms. It is incorrect to add free enthalpy terms for this motion to W_g as given by Volmer.

Dr. W. J. Dunning (*Bristol University*) said : We all recognize the great achievements of Volmer, but we should not, with hindsight, attempt to read into his work more than is there. For example, on p. 97 of his book,[1] Volmer describes a method due to Gibbs for determining the work of formation of a nucleus of radius r_K. One step in this process involves some of the bulk liquid, confined in a cylinder by a piston, being extruded as a droplet through a small orific in the cylinder wall. The work done in forcing out the droplet is given as

$$\int_0^{r_K} (2\sigma/r)4\pi r^2 \, \mathrm{d}r = 4\pi r_K^2 \sigma.$$

This seems to imply that Volmer considered σ, the surface tension, to be independent of the radius which it would not be if the Brownian motion is taken into the surface tension term. It seems that both Volmer and Gibbs were tacitly assuming that the droplet stands still on the orifice. In fact, the still-attached droplet will be bobbing about on the orifice in Brownian motion and at some stage must be liberated to dance away into the vapour space.

The contributions of Kuhrt,[2] Lothe and Pound,[3] Dunning[4] and others analyze the consequences of this last stage of liberation. There is a large measure of common agreement, but where they differ is in their assessment of the magnitude of the so-called replacement factor.[5]

Prof. C. S. Kiang (*Clark College, Atlanta, Ga.*) said: Dunning mentioned various nucleation processes and their roles in his introductory remarks. From our recent studies, we believe that the heteromolecular nucleation (homogeneous or heterogeneous) process should be included as one of the most important nucleation processes for the fogs and smokes formation in the earth's atmosphere. For relative humidity less than 100 %, this nucleation process seems to be the only nucleation mechanism with water in the atmosphere. Most of the primary chemical constituents in the atmosphere do not have low vapour pressures and their atmospheric concentrations are measured in p.p.m. or p.p.b. and are not sufficient to allow nucleation in the gas phase. However, by chemical reactions or radiation or other energy input, secondary products with low volatility can be formed and these reactants may mix with water and undergo heteromolecular nucleation to form new aerosol. For example, at room temperature, SO_2 has vapour pressure around 4 atm. In the presence of oxidants (e.g., $NO_2 + h\nu \rightarrow NO + O$, $SO_2 + O \rightarrow SO_3$, $SO_3 + H_2O \rightarrow H_2SO_4$), H_2SO_4 can be formed. With only 10^{-6} Torr vapour pressure, $H_2SO_4 + H_2O$ will undergo the heteromolecular nucleation to form aqueous sulphuric acid aerosol. After reacting with NH_3, $(NH_4)_2SO_4$ may be formed as stated by Dunning.

[1] M. Volmer, *Kinetik der Phasenbildung* (Steinkopff, Dresden 1939).
[2] F. Kuhrt, *Z. Physik*, 1952, **131**, 185, 205.
[3] J. Lothe and G. M. Pound, *J. Chem. Phys.*, 1962, **36**, 2080.
[4] W. J. Dunning in *Chemistry of the Solid State*, ed. W. E. Garner (Butterworths, 1955), p. 159; *Adsorption et Croissance Cristalline* (Coll. Int. C.N.R.S., Paris, 1965), p. 369.
[5] see W. J. Dunning *Nucleation*, ed. A. C. Zettlemoyer (Marcel Dekker Inc., New York, 1969), pp. 37-47.

Dr. E. R. Buckle (*Sheffield University*) said: The purpose of my paper is to show that on simple kinetic grounds a particle in a volatile aerosol that is homogeneous and isothermal must grow or evaporate in a way that is dictated by the properties of the whole particulate system. The role of coagulation in particle growth is certainly paramount at low temperatures in very dense clouds of ultra-fine particles although for condensation aerosols the centres of coagulation are particles formed during the previous volatile stage.

The properties J, ζ that are characteristic of the particle size distribution are found in the growth and evaporation equations of a particle. For instance, in eqn (2.15), which gives the net rate of increase of material in a particle, the term $\Delta\zeta_{g+1}$ reflects the joint influence of all the particles because its value is related to the size distribution at equilibrium. Now although $\Delta\zeta_{g+1}$ tends to zero for very large clusters the ratio f_{g+1}/f_g is still dependent on J if the processes in the aerosol are occurring naturally. Theoretically, therefore, the communal effects of the particles are unavoidable.

Dr. W. J. Dunning (*Bristol University*) said: Referring to eqn (1)-(5) of Buckle's paper, is it possible to assert at this stage of his argument that there is a limiting value of ω_g as $g \to \infty$? If the clusters are bizarre in form, how the equilibrium between one such monster and another monster behaves as the monsters increase in size can, at present, only be conjectured. At the other extreme, if the clusters were perfect crystals, the equilibrium quotients would oscillate.

Dr. E. R. Buckle (*Sheffield University*) said: In reply to Dunning, if by " monsters " is meant thread-like or branching clusters, especially ones without a centre of symmetry, I would expect them to have little chance of formation by homogeneous processes under the moderate conditions assumed in my paper. They are therefore unlikely to contribute to the formation of stationary states. To prove this it would be necessary to extend the concepts of internal energy fluctuations to include such species. Gaseous ions might interfere in the condensation of heteropolar substances like water to produce elongated structures. For this to have a sensible effect on the condensation process there would have to be very many ions and the gas would be properly regarded as a mixture.

Very large clusters are without influence kinetically and I do not visualize the growth of clusters as ever involving the perfect crystalline state. The size at which a pure particle, with its inherent structural imperfections, is able to assume crystallinity is unknown but it could well be too great for it to have any importance as a rate-determining factor in condensation.

Such considerations are important because they bear on a well-known dilemma of " classical " nucleation theory. In the interpretation of condensation by Volmer theory there is always this element of uncertainty about the physical state of the nucleus : is it solid or liquid? The uncertainty is embarrassing because macroscopically the surface tension has different values for these states and a decision has to be made as to which to use in the theoretical formula. I doubt whether this difference is really meaningful in nucleation.

To overcome this difficulty a theoretical approach is required in which the structures and properties of the condensing particles are related to those of the molecules composing them. As a test of the usefulness of such a theory one would look for its ability to predict the rates of production of the particles and to relate these to measureable physical properties of the system during condensation. A primitive attempt at such a theory was given in ref. (1) of my paper, and Dr. A. A. Pouring and I have been using it in some calculations that should show, among other things, how sensitive the

predictions of the path of condensation are to the molecular details.   Whether the comparison of computed and measured values of experimental variables like pressure and temperature will provide a useful check on the adequacy of the cluster models also remains to be seen.

Dr. D. Stauffer (*Clark College, Atlanta, Ga.*) said: Buckle's eqn (1.9) shows that one can calculate some cluster properties from measured (pressure, density, temperature) relations (equation of state).   Fisher's droplet model [1] gives good agreement with the measured equation of state both near the liquid-gas critical point [2] and at lower temperatures. [3]   It also agrees with direct evaluations of cluster concentrations in a two-dimensional model. [4]   Does Buckle's approach give an alternative droplet model which also can be tested using the measured equation of state?   This would be very valuable as a replacement for the classical nucleation theory.   I would also ask what is the relation between his eqn (2.15) and the " classical " approach (e.g. eqn (10) of Dunham). [5]

Dr. E. R. Buckle (*Sheffield University*) said: In reply to Kiang and Stauffer, I am not optimistic about making comparisons of experimental PV isothermals with theoretical cluster distributions (e.g., my eqn (1.3) and (1.9)) to obtain the properties of the clusters.   Except at high pressures, for which the cluster models are not intended, or at the very high supersaturations which build up in a fast expansion, the concentrations of clusters fall too rapidly with size.   The dependence of the distribution on the external variables should be more apparent experimentally as the system passes through the condensation threshold.   During this stage the Volmer minimum in c_g and the relaxation hump that follows it move into the region of small cluster sizes and then back out again.   The time available for observation is so short that measurements with high time-resolution are called for.   It seems that the measurements should aim to resolve the sizes also if cluster properties are to be investigated.   The results of methods, such as bulk scattering of light, which give only a mean particle size over a finite time interval would be very difficult to relate to such properties because of the complex form of the relaxing size distribution (the curve of c_g against g resembles in shape a PV isotherm of van der Waals at sub-critical temperatures).

In the method of Volmer the clusters in an equilibrium store are assumed to grow by molecular collisions and evaporation is ignored.   The flux condensation is assumed to be that of eqn (2.12), and is therefore independent of cluster size.   Becker and Doering's modification was to consider also evaporation but again there was no allowance for the possibility that the chance of capture or expulsion of molecules might vary with the size of particle.   The theory of my paper shows that the introduction of size-dependent accommodation coefficients leads to the conclusion that the net flux on an aerosol particle is dependent on the size distribution and cannot be calculated from the laws for a macroscopic surface.

Dr. W. J. Dunning (*Bristol University*) said : It seems that the limiting process in Buckle's eqn (1.5) is not general but ancitipates a Volmer-like model in which the clusters are considered to be compact.

[1] *Physics*, 1967, **3**, 255.
[2] *Z. Phys.*, 1970, **235**, 130.
[3] *Phys. Letters*, 1972, **40A**, 345.
[4] *Phys. Rev.*, 1972, **B6**, 2777 ; also *J. Stat. Phys.*, 1972, **6**, 49.
[5] *J. Rec. Atm.*, 1966, **2**, 331.

Dr. E. R. Buckle (*University of Sheffield*) said : In a treatment of this kind there is one respect in which the clusters must be regarded as compact. The stepwise processes $A_{g-1} + A_1 = A_g$, are only amenable to a simple collision theory if the cluster lifetimes are long in comparison with the collision time. High vapour densities are excluded by this, and there is therefore some meaning in concepts such as the cluster-gas interface and the surface tension. It is a point of my paper that if clusters are to exist homogeneously at up to indefinitely large sizes the quantity ζ_g must obey the conditions $\zeta_g > 0$, $\Delta\zeta_g/\Delta g = 0$ in the limit as $g \to \infty$. But this requires $\omega_g \to \omega_\infty$ as $g \to \infty$ where ω_g approaches the constant ω_∞ from below. These conditions are satisfied if one makes the reasonable assumption that, in a growing cluster of iso-tropically bound atoms, the nearest-neighbour coordination number λ_g rises to a limit λ_∞. This represents the ordering process that accompanies the differentiation of the condensed phase.

With regard to the more diffuse entities, only at high vapour densities near the critical point would there be tenuous regions of high local density in significant concentrations. Under such conditions, however, long-range density fluctuations are already a characteristic of the *saturated* vapour and the concepts of nucleation theory are no longer useful.

Prof. M. Kerker (*Clarkson Coll. Techn., Potsdam*) said: With regard to the paper by Buckle, in our experiments on the formation of dibutylphthalate aerosol by cooling a mixture of vapour and NaCl particles (radii ranging from 30 to 100 Å), we observed that only a small fraction of the particles served as condensation nuclei.[1] Also, this number depended strongly upon the rate of cooling ; there were more aerosol particles of smaller average size when the cooling rate was greater. We assumed this was controlled by the rate at which the most effective classes of nuclei could relieve the rapidly increasing supersaturation. Is this observation pertinent to the dynamic processes which Buckle describes in homogeneous nucleation?

Dr. E. R. Buckle (*Sheffield University*) said: In reply to Kerker, if the particles coagulate while still at temperatures at which they are volatile it confirms that their sizes and individual properties are predetermined by the seed and are not influenced by the kinetic factors that determine size distributions in spontaneously-condensed aerosols. Yet the effect predicted for such an aerosol, that the rate of growth of a particle gets slower as its size increases, would lead to what Kerker has observed on changing the cooling rate : the faster the cooling of the vapour, the smaller and more numerous the particles become.

I believe this is purely coincidental, and the effects are characteristic of hetero-geneous nucleation. In experiments on the seeding of water from moist air expanded in the wind tunnel [2] the effectiveness of seed was greatest at low flow rates (i.e., slow cooling) and high humidities. Kerker describes how he makes allowance for the extra time particles have for coagulation if they are moving near the condenser wall. There may also be a connexion between the activity of the NaCl particles as condensa-tion nuclei and their position and speed relative to the wall. The proportion of seed particles that are effective as condensation centres would be expected to be sensitive to the radial velocity and temperature gradients, and therefore to the flow speed. Consequently I suspect the reason for what was observed is the non-uniform condi-tions.

[1] G. N. Nicholson and M. Kerker, *J. Colloid Interface Sci.*, 1973, **43**, 246.
[2] E. R. Buckle and A. A. Pouring, *Nature*, 1965, **208**, 367.

Dr. W. J. Dunning (*Bristol University*) said: With regard to Kiang's paper, how large do the droplets grow before they come to equilibrium with the reduced relative humidity and reduced activity? The authors have pointed out many possible sources of error and complication. Is the activity of, say, sulphuric acid derived from the concentration of sulphuric acid in the vapour phase? Would not this be a composite term including not only H_2SO_4 molecules but other species such as H_3OHSO_4?

It is assumed that the condition of a nucleus of aqueous sulphuric acid is the same as that of a random sample in the bulk solution. However, for bulk solutions, some of the sulphuric acid will be dissociated into ions. In nuclei containing, say, 5 sulphuric acid molecules and perhaps 30 water molecules, such dissociation will be inhibited since some of the resultant electrostatic field will stray outside the nucleus where the dielectric constant is low (~ 1). Further, the ions will tend to avoid approaching the surface of the nucleus and to occupy only the middle; this will affect the entropy of mixing. Such points may need consideration when the theory is developed further.

Dr. R. A. Cox (*AERE, Harwell*) said: With regard to the heteromolecular nucleation of $H_2SO_4 + H_2O$ vapour mixtures discussed in the paper by Kiang and Stauffer, a simple experimental test of the validity of the Flood–Neumann–Doering–Reiss–Doyle theory was suggested by Doyle.[1] His calculations indicated that appreciable nucleation rates would occur at sulphuric acid vapour activities of 10^{-2}-10^{-3} in air at 50 % relative humidity (RH; 25°C). This corresponded to the equilibrium vapour phase activity above an aqueous solution of H_2SO_4 of composition $\simeq 75$ % wt/wt H_2SO_4. Thus a sulphuric acid solution of this composition should fume in air at 50 % RH.

We have measured the concentration of condensation nucleii (CN) in an air-stream passing over concentrated H_2SO_4 solutions of various compositions using a Pollack CN counter. At 72 % wt/wt, no CN were detected even at 70 % RH. With 77 % wt/wt H_2SO_4, particles (300-600 cm^{-3}) were detected at 70 % RH, and at 83 % wt/wt the particle counts at 70 % and 5 % RH were 3×10^5 and 10^4 cm^{-3} respectively.

These experiments are only semi-quantitative since (*a*), the CN counter does not measure the number of nucleating embryos but only the number of particles which grow to sufficient size to register in the CN counter ($\gtrsim 25$ Å). Losses of particles of this size (and smaller) by diffusion to the containing walls will be appreciable. Also (*b*), equilibrium conditions of H_2SO_4 and H_2O vapour were not attained above the liquid surface and the departure from equilibrium cannot be assessed easily. Nevertheless, these results do indicate that the theoretical predictions are not grossly in error and that heteromolecular nucleation in $H_2SO_4 + H_2O$ mixtures can occur at an appreciable rate at extremely low partial pressures of H_2SO_4 vapour (i.e., approximately 10^{-9}-10^{-8} Torr at 50 % RH).

Prof. C. S. Kiang and **Dr. D. Stauffer** (*Clark College, Atlanta*) said: In reply to Dunning, 1-6 Å is a typical radius of the " critical " droplets at the saddle point. After this heteromolecular nucleation, the droplets grow until the H_2SO_4 gas is (nearly) exhausted, which happen for droplet sizes of typically 10-100 Å (see ref. (15) for details).

The H_2SO_4 activity was determined by thermodynamic relations and specific heat measurements (Giauque *et al.*, ref. (6)); the evaluation assumes the presence of only two gaseous species. We do not know the magnitude of the error involved in this approximation. In addition to these dissociation effects, which may differ in small

[1] *J. Chem. Phys.*, 1961, **35**, 795.

droplets from bulk phase dissociation effects, one also expects (ref. (2)) an enrichment of one phase near the droplet surface. For small droplets, the Gibbs adsorption equation describing this surface enrichment can be seriously wrong, in particular if applied to $H_2O + C_2H_5OH$ heteromolecular nucleation. Computer simulations of small liquid droplets (Monte Carlo, molecular dynamics, etc.) might eventually answer these questions; we cannot.

In reply to Cox, for a 72 wt % solution, the H_2SO_4 activity is 0.0007, for 77 % it is 0.0044, and for 83 % it is 0.04 according to Giauque *et al.* (ref. (6)).

Dr. D. Stauffer (*Clark College, Atlanta, Ga.*) said: The vapour pressure of 10^{-4} Torr for H_2SO_4 was questioned by Doyle,[1] who prefers 10^{-6} Torr; which is the better value?

Dr. C. N. Davies (*University of Essex*) said: I agree with Stauffer that there is doubt about the partial pressure of H_2SO_4 above aqueous solutions. It is possible that it could be measured by a technique similar to that described by Frostling.[1] Droplets as large as 2 μm diam. can be kept in suspension, with a greatly reduced loss by sedimentation, in a cylindrical chamber which is continuously rotated. By holding the atmosphere in the chamber at a constant relative humidity and sampling the aerosol over a long period it might be possible to measure the rate of evaporation of H_2SO_4 as a function of the ambient humidity.

Dr. R. G. Picknett (*Chem. Defence Est., Porton Down*) said: I would raise two points about the paper by Davies. The first concerns the evaporation coefficient, which must have a value near to unity if the interpolation formula, eqn (1.13), is to be applicable. Measurements of this parameter are sparse, but a value for water of only 0.04 has been reported, and so eqn (1.13) must be employed with caution. Extensive calculations of droplet evaporation have been made by N. L. Cross and myself in which we find that a 70 % difference in droplet lifetime is obtained when evaporation coefficients of 0.04 and 1.0 are used. This is for drops of 5 μm radius. My second point concerns the effect of self-cooling on the evaporation rate, which Davies correctly states is negligible for the substances other than water in table 2. This effect has also been investigated in the calculations made by N. L. Cross and myself. It is most important for droplet evaporation in vapour-free surroundings, and under these conditions it rapidly becomes significant as the vapour pressure increases above 0.1 mbar. If we take a vapour pressure of 1 mbar, 10 times as large, then a 5 μm radius droplet of a typical organic liquid will have the surface temperature depressed by about 0.3°C, i.e., sufficient to cause a material reduction in the rate of evaporation.

Dr. C. N. Davies (*University of Essex*) said: In reply to Picknett, it is difficult to measure the evaporation coefficient, α. Bradley *et al.*[2] gave 0.28 for di-n-butyl phthalate and 0.35 for butyl stearate droplets in air but it was subsequently decided that $\alpha \approx 1$ for di-n-butyl phthalate in air, hydrogen and freon,[3] for straight chain hydrocarbons in air,[4] and for branched-chain hydrocarbons and a straight-chain fluorocarbon in air.[5] For rhombic sulphur it was found that $\alpha = 0.73$.[6]

[1] *J. Aerosol Sci.*, 1970, **1**, 341 ; and 1973, in press.
[2] R. S. Bradley, M. G. Evans and R. W. Whytlaw Gray, *Proc. Roy. Soc. A*, 1946, **186**, 368.
[3] J. Birks and R. S. Bradley, *ibid.*, 1949, **198**, 226.
[4] R. S. Bradley and A. D. Shellard, *ibid.*, 1949, **198**, 239.
[5] R. S. Bradley and G. C. Waghorn, *ibid.*, 1951, **206**, 65.
[6] R. S. Bradley, *ibid.*, 1951, **205**, 553.

Alty and Mackay [1] concluded that thermal accommodation of water vapour molecules striking a water surface was achieved but that the rate of re-evaporation of condensing molecules was high at vapour equilibrium so that the rate of evaporation of water molecules from the liquid phase was only 0.034-0.036 of the rate of impact from saturated vapour, according to kinetic theory. However, Jamieson,[2] using a dynamic technique, found α to be at least 10 times greater than this low value.

There has thus been a tendency for α for liquids to increase as experimental techniques improved and, recently, Jer Ru Maa,[3] using a jet tensimeter, has obtained results which lead him to conclude that $\alpha = 1$ for all liquids. Further references are given in table 1.8 of A. G. Amelin's book *Theory of Fog Condensation* (Moscow, 1972). Picknett's remarks on evaporation are interesting. For water, the temperature of a drop, regardless of its size, is equal to that of the ventilated wet bulb thermometer.

Prof. E. Rosner (*Yale University*) said: While the evaporation (or condensation) coefficient α for the *liquids* of interest to Davies may indeed be close enough to unity to ensure the utility of eqn (1.12), this assumption would certainly fail for the evaporation (or growth) of *crystalline* aerosols, especially when the dominant vapour species do not exist as structural entities in the condensed phase.[4] For example, low and sharply temperature dependent α-values have been measured for the individual faces of crystalline solids which (i) *dissociate* upon sublimation (e.g., $AlN(s)$, $Al_2O_3(s)$, $NH_4Cl(s)$), or (ii) whose vapours are *associated* ($As(s)$ and $P(s)$, giving tetramers in the vapour phase). Also of interest in this connection is the fact that for such solids melting is expected to be accompanied by a discontinuous increase (" jump ") in α (observed [5] for the sublimation of polycrystalline $Al_2O_3(s)$, $Ga_2O_3(s)$ and $3Al_2O_3$-$2SiO_2(s)$). Since this is probably a general phenomenon holding for phase changes even below the equilibrium transition temperature, it is interesting to consider its consequences for the relative evaporation (or growth) of aerosols for which the condensed phase may be either crystalline or amorphous. In the usual case for which $\Delta H_{\text{sublim}} > \Delta H_{\text{vap}}$. both high vapour pressure and high α would combine to cause rapid gasification of a liquid aerosol compared to its crystalline counterpart at the same surface temperature. For condensational growth from the vapour, however, these effects would oppose one another, causing loss disparity in condensation rates more than in gasification rates. Finally, since compact crystalline *aggregates* appear to be present (at least as intermediates) during the production of inorganic oxide aerosols in flames we should note that prior to complete sintering such an aggregate (i) would be characterized by an effective α higher than that corresponding to the surfaces of its crystalline constituent " primary " particles (owing to multiple vapour molecule/solid encounters during escape of condensation from/in the " labyrinth "); (ii) can lose or gain mass without a corresponding change in the *outer* dimensions of the aggregate (owing to a change in overall aggregate density, ρ).

Dr. C. N. Davies (*University of Essex*) said: Rosner had made some important points. However, the association of vapour molecules to form, e.g., tetramers will

[1] T. Alty and C. A. Mackay, *ibid.*, 1935, **149**, 104.

[2] D. T. Jamieson, *Nature*, 1964, **202**, 583.

[3] Jer Ru Maa, *Ind. Eng. Chem. Fund.*, 1967, **6**, 504 ; 1970, **8**, 564 ; 1970, **9**, 283.

[4] This has been reviewed by G. A. Somorjai and J. E. Lester in *Progress in Solid State Chemistry*, H. Reiss, ed. (Pergamon Press, Oxford, 1967), Vol. 4, pp. 1-52.

[5] R. P. Burns, J. Jason and M. G. Inghram, *J. Chem. Phys.*, 1964, **40**, 2739 ; see also R. P. Burns, *Ph.D. Dissertation* (Dept. Physics, Univ. Chicago, 1965).

reduce the kinetic impact rate by $\frac{1}{8}$ so that a corresponding reduction in the rate of vaporization occurs, quite apart from any effect due to α. If the vapour is dissociated, the impact rates of each type will usually differ so that the values of α need to adjust themselves accordingly.

Prof. M. Kerker (*Clarson Coll. Techn., Potsdam*) said: I would ask Davies, how would one transpose this calculation to a heterodisperse aerosol, assuming condensation to the wall was minimal and that the process was primarily distillation from smaller to larger particles due to the Kelvin effect? What would the vapour field " seen " by a particular particle be? How would the evaporization rate compare to that for the single particle model? Further questions are: (i) how sensitive would the evaporation rate be to the evaporation coefficient, particularly for small concentration gradients? (ii) Would one expect that " contamination " might significantly affect evaporation rates? (iii) May one neglect the latent heat effects, particularly in an aerosol having a particle concentration of the order of 10^6 particles cm^{-3}?

Dr. C. N. Davies (*University of Essex*) said: The vapour field " seen " by a particle depends on Kn. When Kn is large the particle " sees " a vacuum, roughly up to a distance Kna from its centre. When Kn is very small the concentration gradient outside the particle is such that

$$(n_r - n_\infty)/(n_s - n_\infty) = a/r,$$

where n_r is the concentration of vapour at radius r.

If the concentration of the aerosol is 10^6 particles/cm^3, then the volume per particle averages 10^{-6} cm^3, which is equal to a sphere of radius 62 μm. During quasi-steady evaporation of an isolated particle having $a = 0.31$ μm the concentration at the surface of a concentric sphere of radius 62 μm would be 99.5 % of the concentration at infinity. The evaporation under quasi-steady conditions of such a particle in an aerosol of 10^6 particles cm^3 therefore proceeds at the same rate as it would were the particle isolated. The establishment of quasi-steady conditions requires a time of the order of $\lambda/\bar{c}$, say, 10^{-10} s when Kn is large; for diffusion controlled evaporation the time dependent term is $a/\sqrt{\pi\nabla t}$. Putting this equal to 0.01, so that the difference between the transient and quasi-steady rates of evaporation is negligible, gives $t = 10^{-4}$ s. Whatever the value of Kn, the time taken to establish quasi-steady conditions is negligible; the rate of evaporation of a particle in the cloud will be the same as that of an isolated particle.

If the coefficient α is very small, the rate of evaporation is not controlled by diffusion but by the rate of escape of vapour molecules from the surface, even though Kn may be very small. This happens when water droplets are coated with a layer of long chain molecules.[1] As α decreases, therefore, the rate of evaporation becomes less dependent on the concentration gradient and more dependent on $\alpha/$Kn; such behaviour is unlikely to occur with drops of organic liquids.

Contamination can affect the evaporation of liquid droplets in two ways: (i) by lowering the vapour pressure due to the rising concentration of involatile contaminant as evaporation proceeds; (ii) by forming a film on the surface of aqueous drops which impedes evaporation; highly specific properties are required in the contaminant for this effect to be large.

Suppose the concentration of aerosol is 7.7×10^{-7} g/cm^3; the latent heat of vaporization of DBP is 79 cal/g so that complete evaporation will withdraw from the

[1] C. N. Davies, *Disc. Faraday Soc.*, 1960, **30**, 144.

gas phase 6.1×10^{-5} cal/cm³. 1 cm³ of air has a heat capacity of 3×10^{-4} cal/°C. The fall in temperature due to complete evaporation of the disperse phase is thus $3 \times 10^{-4}/6.1 \times 10^{-5} = 4.9$°C.

Dr. R. G. Picknett (*Chem. Defence Est., Porton Down*) said: Kerker has asked what happens to the evaporation process when a cloud of droplets is present. N. L. Cross and myself have performed calculations for monodisperse aerosols which we hope to publish soon. Provided the mass concentration of aerosol is less than about 1 mg/m³, interaction of the vapour gradients adjacent to neighbouring droplets is negligible, and the only effect of the aerosol is to increase the background vapour concentration as the evaporation proceeds, thus slowing the process.

Prof. M. Kerker (*Clarkson Coll. Techn., N.Y.*) said: We have found our aerosols quite stable to evaporation as pointed out in the discussion on our paper. Since the mass concentration is 1 mg/l., the evaporation must proceed even significantly lower than Cross finds at 1 mg/m.

Prof. D. E. Rosner (*Yale University*) said: In quantitative treatments of the evolution of the aerosol size spectrum function $n(r, \mathbf{x}, t)$ under conditions for which the " growth " term $\partial(\dot{r}n)/\partial r$ plays an important role, it is common to assume that the individual particle growth rate $\dot{r}$ is a function of, at most, the prevailing particle radius r and local environmental variables at position $\mathbf{x}$ and time t. For example, in the continuum limit (Kn $\ll 1$) the Maxwell–Smoluchowski equation provides the proportionality $\dot{r} \propto r^{-1}$, but it is prudent to recall the assumptions underlying this simple result prior to its formal application to dilute (low volume fraction) aerosols in new situations. In a recent investigation [1] of the vaporization of isolated droplets in the continuum regime, conditions leading to the breakdown of the instantaneous $\dot{r} \propto r^{-1}$ law have been explored, with some results of potential significance to aerosol science/technology mentioned here. Briefly, for the validity of the $\dot{r} \propto r^{-1}$ law it is not sufficient that droplet and its local environmental conditions undergo negligible fractional changes in the characteristic diffusion time r^2/D_v (where D_v is the Fick diffusion coefficient for the evaporating/condensing vapour). It is also necessary that the velocity of the moving phase boundary be small compared to the characteristic vapour diffusion velocity. This leads to a necessary condition of the form :

$$\frac{\rho_\infty}{\rho_{\text{droplet}}} \left| \frac{\omega_{v,w} - \omega_{v,\infty}}{1 - \omega_{v,\omega}} \right| \ll 1,$$

where $\omega_{v,w}$ is the vapour mass fraction at the droplet surface and $\omega_{v,\infty}$ is the vapour mass fraction in the gaseous environment " far " from (i.e. several droplet radii away from) the droplet.[2] Ordinarily, the density ρ_∞ of the gaseous environment is much smaller than the density ρ_{droplet} of the droplet itself, and the local vapour mass fractions, ω_v, are everywhere much smaller than unity so that this condition for the validity of the quasi-steady approximation (leading to $\dot{r} \propto r^{-1}$) is satisfied. However, if one considers a spray of a liquid fuel, say, at a total pressure level comparable to the

[1] D. E. Rosner and W. S. Chang, *Combustion Sci. Techn.*, 1973, in press.
[2] Under conditions for which the Maxwell–Smoluchowski $\dot{r}$ expression is valid, the diffusional " driving force " parameter in the absolute value brackets is itself small compared to unity, and $-\dot{r}$ is linearly proportional to $\omega_{v,w} - \omega_{v,\infty}$. However, a generalization of the quasi-steady Maxwell–Smoluchowski expression is available for which the $\dot{r} \propto r^{-1}$ dependence is preserved even when the driving force parameter is not small. (See, e.g. D. B. Spalding, *Convective Mass Transfer—An Introduction* (McGraw-Hill, New York, 1963)).

GENERAL DISCUSSION

thermodynamic critical pressure of the fuel, then for droplets whose temperature approaches their critical temperature this parameter becomes appreciable, and the quasi-steady approximation loses its utility. Interestingly enough this situation is encountered for diesel engine cylinders [1] into which kerosene ($p_c \approx 26$ atm, $T_c \approx 662$ K) is injected as a droplet spray. In such cases a fully transient treatment of the $\dot{r}$ function appearing in the aerosol evolution equation is evidently required.

[1] D. E. Rosner, *AIAA J.*, 1967, **5**, 163.