

# HETEROGENEOUS NUCLEATION BY AGGREGATES OF PARTICLES

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## Summary

The induction of a new phase by fine particles of a nucleating substance is complicated not only by variation in sizes but also by aggregation. The general effect of aggregation is to decrease the total number of particles but to reduce the supercooling (or supersaturation) necessary for growth of a new phase. Point contacts appear to be more fruitful than do line contacts, although both may be able to cause a substance to be more active than a large flat surface of the substrate. If the contact between particles is not a specially favoured position for nucleation, the aerosol as a whole appears to contain a higher proportion of active particles because of the persistence of initially active particles and the loss of less active ones.

## I. INTRODUCTION

The nucleation of supersaturated solutions and vapours and of supercooled liquids by foreign particles depends upon the size and composition of the particles. Fletcher (1958) has related the extent of supersaturation or supercooling to the radii of spherical nuclei and the contact angle between the phases formed on their surfaces. In any practical work involving aerosols, particularly in the laboratory, it is necessary to use such concentrations that particles coagulate. Thus typical aerosols of silver iodide used in other studies in this laboratory contained  $10^5$  particles  $\text{cm}^{-3}$  (approximate mean radius  $10^{-6}$  cm), the concentration of which would fall by coagulation and by diffusive loss to the walls of the containing vessel to about one-third in an hour. Frequently it was necessary to study aerosols over periods longer than this when the effectiveness of the nuclei are being altered by the action of chemicals or of light. This paper examines theoretically the effect of coagulation.

## II. FORM OF AGGREGATES

If the particles are spherical and of equal size, the aggregates form simple chains or structures with point contacts (Fig. 1 (a)). We shall confine this portion of our discussion to dimers. If the particles are crystals then the form of the aggregates is more complex. Only one situation will be examined: that of two crystals forming a step (Fig. 1 (b)).

At edges or points of contact between surfaces the growth of a new phase will usually be enhanced by capillary condensation because of the favourable curvature of the surface of the phase being formed. If, however, the growing phase is crystalline then its fit on both of the surfaces forming the aggregate may become dominant. Thus in Figure 1 (b) it may be imagined that the substrate

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for crystal nucleation may be suitable on the horizontal surface but unsuitable on the vertical surface. Under these conditions the aggregate may exhibit the characteristics only of the more active member of the pair. Such an aggregate shall be defined as "not in registry". For the formation of a liquid phase the surfaces are always in registry.

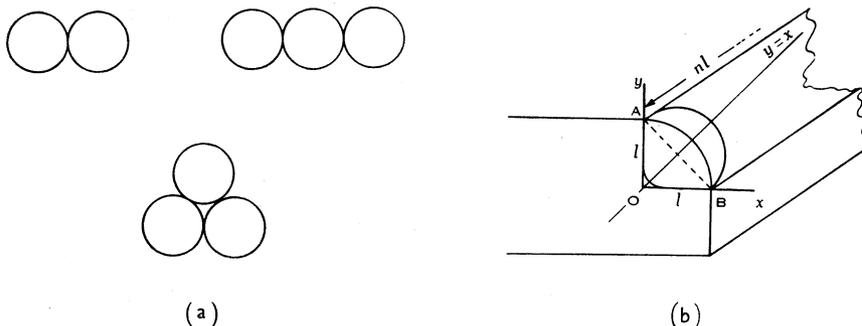


Fig. 1.—Forms of aggregates. (a) Aggregates from spheres, (b) stepped aggregates from plates.

### III. PROPERTIES OF AGGREGATES NOT IN REGISTRY

Consider an aerosol containing  $p$  single particles in each of  $n$  classes. These classes may be determined experimentally by lowering the temperature or increasing the supersaturation by measured amounts, the less active particles acting only under the greater driving force. At a given time we shall want to know how many monomers, dimers, trimers, etc. are present and to classify these aggregates on their probable composition. If a polymer contains at least one particle from class 1 (the most active), then it shall continue to belong to class 1. If, however, the most active particle in the polymer belongs to class  $r$  then the aggregate belongs to class  $r$ . Aggregation therefore decreases the total number of particles and eliminates the least active classes.

The kinetics of coagulation under Brownian movement was formulated by Smoluchowski (1916, 1917) on the basis that all particles are the same size and that all aggregates are regarded as having the same size and diffusion constant as the single particles.

The rate of removal of particles is given by

$$-dv/dt = kv^2, \dots\dots\dots (1)$$

where  $k$ , the velocity constant, is defined in terms of the viscosity of the gas, the radius of particle, its sphere of influence, and the temperature (see Green and Lane 1957).

The total number of aggregates and single particles after a time  $t$  is

$$\Sigma v = np\{1/(1+T)\}, \dots\dots\dots (2)$$

where  $T$  is  $knpt$  and  $\Sigma v$  is the sum of single particles ( $v_1$ ), dimers ( $v_2$ ), trimers ( $v_3$ ),  $m$ -mers ( $v_m$ ). The number of  $m$ -mers is

$$v_m = npT^{m-1}/(1+T)^{m+1}. \dots\dots\dots (3)$$

We now require the composition of each aggregate in terms of the probable most active monomer in it. Suppose we select  $m$  particles at random to form an  $m$ -mer. Since there are  $np$  particles, the number of different choices is

$$\binom{np}{m}.$$

The number of choices containing only particles from classes  $r+1, r+2, \dots, n$  is

$$\binom{np-rp}{m}$$

and the number containing only particles from classes  $r, r+1, \dots, n$ , is

$$\binom{np-rp+p}{m}.$$

Thus the number containing only particles from groups  $r, r+1, \dots, n$ , and at least one particle from group  $r$  is the difference of these numbers, is

$$\binom{np-rp+p}{m} - \binom{np-rp}{m}.$$

Since these and only these choices form  $m$ -mers which belong to class  $r$ , the fraction of the  $m$ -mers which belongs to class  $r$  is

$$F_{mr} = \left\{ \binom{np-rp+p}{m} - \binom{np-rp}{m} \right\} / \binom{np}{m}. \quad \dots \dots \dots (4)$$

In any experiment the total number of particles within any one class is large and the number of particles within an aggregate small. Under these conditions

$$\binom{q}{m} \simeq \frac{q^m}{m!}$$

so that (4) becomes

$$\begin{aligned} F_{mr} &= \frac{(np-rp+p)^m/m! - (np-rp)^m/m!}{(np)^m/m!} \\ &= \frac{(n-r+1)^m - (n-r)^m}{n^m}. \quad \dots \dots \dots (5) \end{aligned}$$

Equation (3) gives the number of each polymer at a given time and the total number of particles active in a given temperature class  $r$  is then

$$A_r = \nu_1 F_{1r} + \nu_2 F_{2r} + \nu_3 F_{3r} + \dots + \nu_m F_{mr}. \quad \dots \dots \dots (6)$$

A sample is considered containing five classes and their distribution between classes 1 to 5 (expressed as a percentage of the current number of particles) is shown in Figure 2. The percentage active at any temperature step for aggregates up to 16 particles is shown in Figure 3, which illustrates the steady march of the

sample into the most active class. When the total concentration of the sample has decreased to 20 per cent. of its original value ( $T=4$ , Fig. 2) the first temperature class has increased from 20 to 55 per cent.

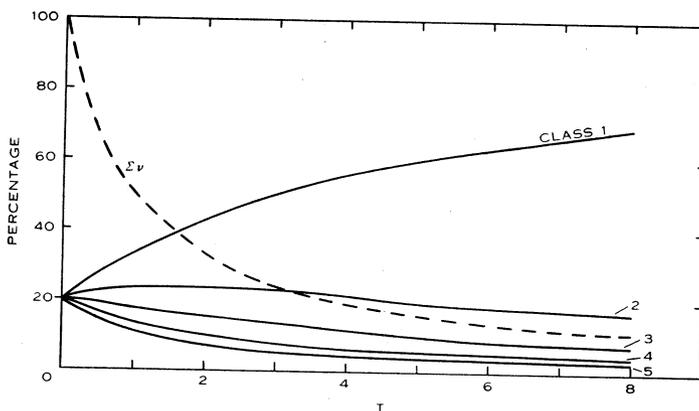


Fig. 2.—The variation with time ( $T=knpt$ ) of the total number of particles and of their distribution between classes 1-5 (expressed as a percentage of the current number of particles).

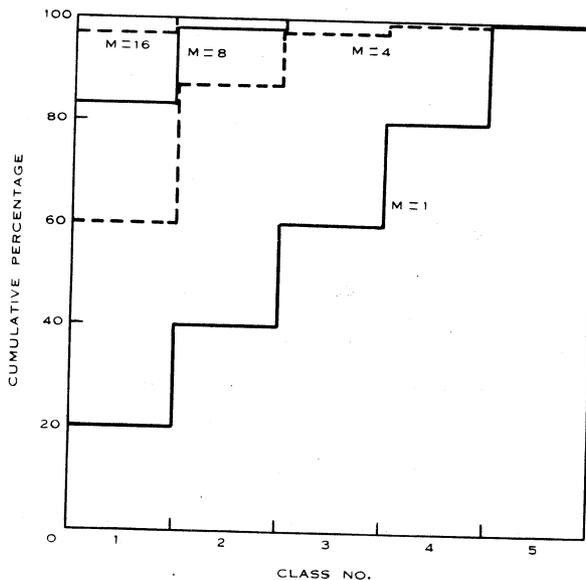


Fig. 3.—The percentage active at given temperature ranges for aggregates containing  $m$  particles. Any particle active at the higher temperature (e.g. class 1) will also be active at a lower temperature (e.g. class 5).

#### IV. PROPERTIES OF SPHERICAL DIMERS IN REGISTRY

Let the aerosol consist of particles each of two spheres of radius  $R$  (Fig. 4). Let the surface of the condensed phase lying between the spheres be generated by a function  $y=f(x)$ . We require that the surface free energy be a minimum

for a given volume  $V$  of condensed phase. Let the angle of contact, measured through the condensed phase, be  $\theta$ . Then the difference in free energy between the system with and without a volume  $V$  of condensed phase is

$$\Delta G = V\Delta G_V + S_{12}\gamma_{12} - S_{23}\gamma_{13} + S_{23}\gamma_{23}, \dots \dots \dots (7)$$

where the  $S$  and  $\gamma$  are the surface areas and surface energies between the phases 1, 2, 3 as indicated.  $\Delta G_V$  is the free energy of transformation from one phase to

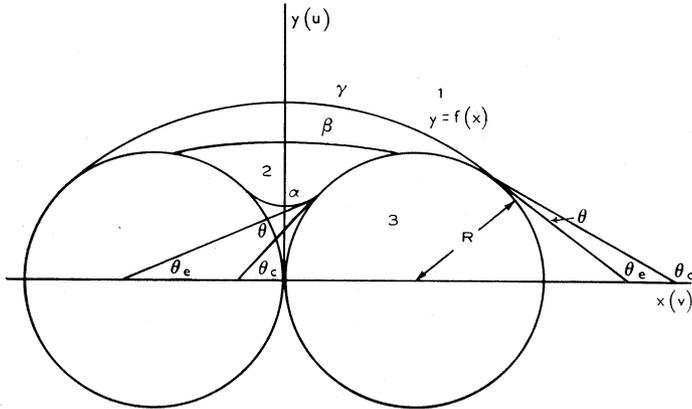


Fig. 4.—Formation of a new phase (2) from the initial (1) on a nucleus (3) formed from two particles each of radius  $R$ .  $\theta$ =contact angle;  $\tan \theta_c$ =tangent to the generating circle;  $\tan \theta_e$ =tangent to the generating curve  $y=f(x)$ .

- $\alpha$ : a minimum at  $x=0$ ,  $\tan \theta_c > 0$ ,  $\tan \theta_e > 0$ ;
- $\beta$ : a maximum at  $x=0$ ,  $\tan \theta_c > 0$ ,  $\tan \theta_e < 0$ ;
- $\gamma$ : a maximum at  $x=0$ ,  $\tan \theta_c < 0$ ,  $\tan \theta_e < 0$ .

another. The relation between contact angle and interfacial energies is assumed to be

$$\gamma_{12} \cos \theta = \gamma_{13} - \gamma_{23}. \dots \dots \dots (8)$$

The volume and surface areas are

$$\left. \begin{aligned} V &= 2\pi \int_0^{x_0} y^2 dx - \frac{2}{3}\pi x_0^2(3R - x_0), \\ S_{12} &= 4\pi \int_0^{x_0} y(1 + y_x^2)^{\frac{1}{2}} dx, \\ S_{23} &= 4\pi R x_0, \end{aligned} \right\} \dots \dots \dots (9)$$

where  $y_x$  is  $dy/dx$ .

Hence we require that  $\Delta G$ , given by

$$\Delta G = 2\pi \int_0^x [\Delta G_V(y^2 - 2xR + x^2) + 2\gamma_{12}\{y(1 + y_x^2)^{\frac{1}{2}} - R \cos \theta\}] dx \dots \dots \dots (10)$$

shall be a minimum. This condition is obtained from

$$\frac{\partial K}{\partial y} - \frac{d}{dx} \frac{\partial K}{\partial y_x} = 0, \dots \dots \dots (11)$$

where  $K$  is the integrand of equation (10).

This leads to

$$y_{xx}(1+y_x^2)^{-3/2} - y^{-1}(1+y_x^2)^{-1/2} = \Delta G_V / \gamma_{12} = \zeta, \quad \dots \quad (12)$$

which is equivalent to

$$-\frac{d}{dy}\{y(1+y_x^2)^{-1/2}\} = \zeta y,$$

that is,

$$(1+y_x^2)^{-1/2} = 1/\xi y - \frac{1}{2}\zeta y, \quad \dots \quad (13)$$

where  $\xi$ , the integration constant, is determined from the condition that

$$\left. \begin{aligned} y_x = 0 \text{ at } x=0 \quad (y=y_0), \\ \xi = 1/y_0(1+\zeta y_0). \end{aligned} \right\} \quad \dots \quad (14)$$

The solution of (13) must be written in several forms depending upon the value of  $\zeta$ .

Case (i)  $\zeta > 0$  (subsaturation)

The gradient of the generating curve is everywhere positive and the curve has a minimum at  $x=0$ . Equation (14) requires  $\xi > 0$  since  $\zeta, y_0 > 0$ . Integration of equation (13) gives

$$\int_{y_0}^y \frac{dy}{\{\xi^2 y^2 / (1 - \xi \zeta y^2) - 1\}^{1/2}} = \int_0^{x_0} dx, \quad \dots \quad (15)$$

where  $y_0$ , the value of  $y$  for  $x=0$ , is found by solving equation (13) with  $y_x$  equal to zero, that is,

$$y_0 = \{-\xi + (\xi^2 + 4\xi\zeta)^{1/2}\} / 2\zeta\xi. \quad \dots \quad (16)$$

This equation transforms to

$$(ab)^{1/2} \cdot v = \int_f^{Rz/(ab)^{1/2}} \frac{(1-z^2)dz}{\sqrt{\{(e^2-z^2)(z^2-f^2)\}}}, \quad \dots \quad (17)$$

where

$$\left. \begin{aligned} v = x/R, \quad z = (ab)^{1/2}y, \\ e^2 = (b/2a + 1) + (b^2/4a^2 + b/a)^{1/2}, \\ f^2 = (b/2a + 1) - (b^2/4a^2 + b/a)^{1/2}, \\ a = \zeta R, \quad b = \xi R. \end{aligned} \right\} \quad \dots \quad (18)$$

This may be evaluated in terms of elliptic integrals

$$\left(\frac{ab}{e^2}\right)^{1/2} v = \frac{1}{e^2} \{F(k, \frac{1}{2}\pi) - F(k, \varphi)\} - \{E(k, \frac{1}{2}\pi) - E(k, \varphi)\}, \quad \dots \quad (19)$$

where  $F(k, \frac{1}{2}\pi), E(k, \frac{1}{2}\pi)$  are the complete elliptic integrals of the first and second kinds,  $F(k, \varphi), E(k, \varphi)$  are incomplete elliptic integrals, and

$$\left. \begin{aligned} \sin \varphi = (1/k)(1-abu^2/e^2), \\ k^2 = (e^2 - f^2)/e^2, \\ u = y/R. \end{aligned} \right\} \quad \dots \quad (20)$$

The parameter  $b$  is determined from the condition that the curve shall intersect the circles (see Fig. 4, curve  $\alpha$ ) at an angle  $\theta$  (the contact angle). If  $\tan \theta_e$  is the gradient to the elliptic curve and  $\tan \theta_c$  that to the circle, then  $\theta_e = \theta_c - \theta$ , and

$$\begin{aligned} \tan \theta_e = y_x &= \{b^2 u_i^2 / (1 - ab u_i^2)^2 - 1\}^{\frac{1}{2}} = \tan \overline{\theta_c - \theta} \\ &= \frac{(1 - v_i) / u_i - \tan \theta}{1 + (1 - v_i) \tan \theta / u_i} = \varepsilon, \end{aligned} \quad \dots \dots \dots (21)$$

where  $(u_i, v_i)$  is the point of intersection of the generating curve. Therefore

$$b = (\varepsilon^2 + 1)^{\frac{1}{2}} / \{u_i + a u_i^2 (\varepsilon^2 + 1)^{\frac{1}{2}}\}. \quad \dots \dots \dots (22)$$

Case (ii)  $\zeta = 0$  (saturation)

Reverting to equation (12) then

$$y_{xx}(1 + y_x^2)^{-1} - y^{-1} = 0, \quad \dots \dots \dots (23)$$

the solution to which is

$$u = (1/b) \cosh bv, \quad \dots \dots \dots (24)$$

where

$$b = (1/v_i) \operatorname{arsinh} (1/\varepsilon), \quad \dots \dots \dots (25)$$

and  $\varepsilon$  is defined in equation (21).

Case (iii)  $\zeta < 0$  (supersaturation)

Put  $a = -c$  where  $c > 0$ . It may be shown that  $b$  must be greater than 0. Three cases arise, shown in Figure 4, and equation (17) becomes

$$(ac)^{\frac{1}{2}} v = \int \frac{(1 + z^2) dz}{\sqrt{\{(e^2 - z^2)(z^2 - f^2)\}}}. \quad \dots \dots \dots (26)$$

( $\alpha$ ) A minimum at  $x = 0$ ,  $\tan \theta_c > 0$  (Fig. 4, curve  $\alpha$ ).

The solution is

$$\left(\frac{bc}{e^2}\right)^{\frac{1}{2}} v = \left(\frac{1}{e^2}\right) \{F(k, \frac{1}{2}\pi) - F(k, \varphi)\} + \{E(k, \frac{1}{2}\pi) - E(k, \varphi)\}, \quad \dots (27)$$

where

$$\left. \begin{aligned} e^2 &= (b/2c - 1) + (b^2/4c^2 - b/c)^{\frac{1}{2}}, \\ f^2 &= (b/2c - 1) - (b^2/4c^2 - b/c)^{\frac{1}{2}}, \\ k^2 &= (e^2 - f^2)/e^2, \\ \sin \varphi &= \frac{1}{k} \left(1 - \frac{bc}{e^2} u^2\right)^{\frac{1}{2}} \\ &= \left\{ \frac{b^2 u_i^2}{(1 + bc u_i^2)^2} - 1 \right\}^{\frac{1}{2}} = \frac{(1 - v_i) / u_i - \tan \theta}{1 + (1 - v_i) \tan \theta / u_i}, \\ b &= \frac{(\varepsilon^2 + 1)^{\frac{1}{2}}}{bc u_i^2 (\varepsilon^2 + 1)^{\frac{1}{2}} - u}. \end{aligned} \right\} \dots \dots (28)$$

When  $\varphi$  is close to  $\frac{1}{2}\pi$  the differences of the tabulated functions cease to be accurate. The differences are then expanded by Taylor's theorem about  $\frac{1}{2}\pi$

(β) A maximum at  $x=0$  and  $\tan \theta_c > 0$  (Fig. 4, curve β).

The equation to be solved is

$$(bc)^{\frac{1}{2}}v = - \int \frac{(1+z^2)dz}{\sqrt{\{(e^2-z^2)(z^2-f^2)\}}}, \dots\dots\dots (29)$$

and the solution is

$$\left(\frac{bc}{e^2}\right)^{\frac{1}{2}}v = \frac{1}{e^2}F(k, \varphi) + E(k, \varphi), \dots\dots\dots (30)$$

where the various symbols are given by equation (28).

(γ) A maximum at  $x=0$  and  $\tan \theta_c < 0$  (Fig. 4, curve γ).

The solution is given by equations (30) and (28).

Case (iv)

A special case arises when  $\theta_c=0$ . The curve becomes a straight line given by

$$u = (bc)^{-\frac{1}{2}}. \dots\dots\dots (31)$$

Case (v)

A special case arises when  $b$  becomes infinite, i.e. if the intersection of curve and circle is given by  $1-cu(e^2+1)^{\frac{1}{2}}=0$ . The curve becomes a circle given by

$$u^2 + v^2 = 1/c^2. \dots\dots\dots (32)$$

(a) Calculation of the Form of the Liquid Surface

The calculations are confined to the substances silver iodide and water. The contact angle for AgI/Liquid H<sub>2</sub>O/H<sub>2</sub>O (vap.) is 10°. It is assumed, following Fletcher, that this angle applies whether the phases are ice/vapour or ice/water, although this is very doubtful. It does, however, enable a comparison to be made with the curve for spherical particles obtained by Fletcher's method (1958).

We are interested in supersaturated conditions so that no calculations were made in the under-saturation region. The procedure in calculation was to take a point ( $u_i, v_i$ ) on the generating circle representing the particle and then to determine  $c$  by successive approximations from either of equations (27) or (30). Equations (24), (31), and (32) enable three curves to be calculated explicitly and give a guide to choice of  $c$  values for the approximative methods. The results of calculation are shown in Figure 5. It will be noticed that the  $c$  values rise to a maximum and then fall: there are two surfaces for each  $c$  value ( $-\Delta G_V/\gamma_{12}$ ).

(b) The Free Energy of Embryos

The theory of nucleation of a new phase on a substrate requires that transient groups of molecules (embryos) form on the surface. The relatively large free surface energies of the smaller embryos cause these to be unstable: the number present of each size at a given temperature and supersaturation may then be determined from Boltzmann's law. With increasing size the free energy barrier rises to a maximum and once an embryo exceeds a critical size, it grows without

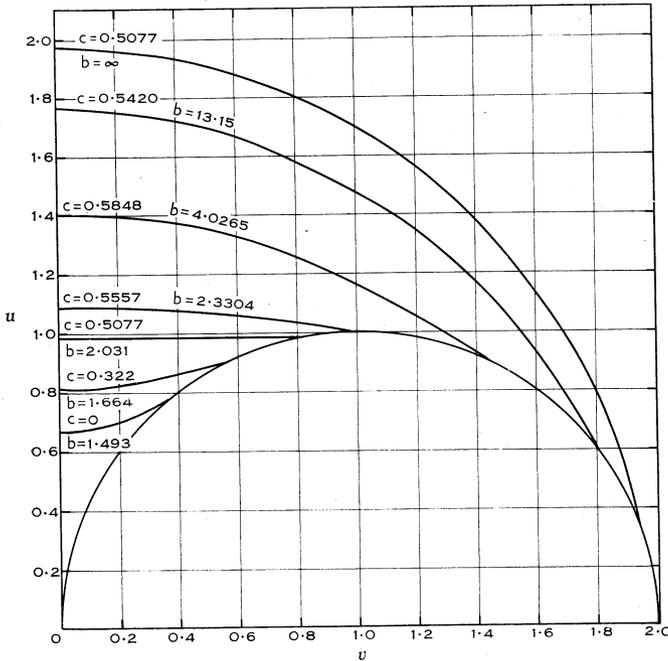


Fig. 5.—Shapes of the menisci from saturation ( $c=0$ ) through increasing supersaturation ( $c$  increasing):  $\theta=10^\circ$ , generating circle of unit radius.

limit. Equation (10) expresses the contributions of the free energy changes due to surface and to phase transformation and may be rewritten as

$$\begin{aligned}
 \Delta G &= 2\pi\Delta G_v R^3 \int_0^{v_i} u^2 dv - \frac{2}{3}\pi\Delta G_v R^3 v_i^2 (3 - v_i) \\
 &\quad + 4\pi\gamma_{12} R^2 \int_0^{v_i} u(1 + u_v^2)^{\frac{1}{2}} dv - 4\pi\gamma_{12} R^2 v_i \cos \theta \\
 &= -\frac{2}{3}\pi\Delta G_v R^3 v_i^2 (3 - v_i) - 4\pi\gamma_{12} R^2 v_i \cos \theta \\
 &\quad + 2\pi\Delta G_v R^3 \int_{u_0}^u \frac{u^2}{u_v} du \\
 &\quad + 4\pi\gamma_{12} R^2 \int_{u_0}^u \frac{u(1 + u_v^2)^{\frac{1}{2}}}{u_v} du. \dots\dots\dots (33)
 \end{aligned}$$

Since  $u_v$  is known as a function of  $u$  only (equation (13)), the solution may be obtained.

The integrals may be written into a combination of the forms

$$\int \frac{dz}{\sqrt{\{(e^2 - z^2)(z^2 - f^2)\}}} \quad \int \frac{z^2 dz}{\sqrt{\{(e^2 - z^2)(z^2 - f^2)\}}} \quad \int \frac{z^4 dz}{\sqrt{\{(e^2 - z^2)(z^2 - f^2)\}}}$$

The first of these integrals gives an elliptic integral of the first kind ; the second integral gives an elliptic integral of the second kind. The third integral is reduced by using the relation

$$z\sqrt{Z} = \int \frac{dz}{\sqrt{Z}} - 2(1+k^2) \int \frac{z^2}{\sqrt{Z}} dz + 3k^2 \int \frac{z^4}{\sqrt{Z}} dz, \dots \quad (34)$$

where  $Z$  is the denominator in the integrals above and  $k$  is the modulus of the elliptic integral (defined in equations (20) and (28)).

The final expressions for the free energies are : \*

Case (ii) :  $a=0$

$$\Delta G = -\frac{2}{3}\pi\Delta G_V R^3 v^2 (3-v) - 4\pi\gamma_{12} R^2 v \cos \theta + \{ \pi\gamma_{12} R^2 / b^2 - \pi\Delta G_V R^2 / 2b^3 \} (2vb + \sinh 2vb). \dots \quad (35)$$

Case (iii $\alpha$ ) :  $a=-c$ , minimum at  $x(v)=0$

$$\begin{aligned} \Delta G = & -\frac{2}{3}\pi\Delta G_V R^3 v^2 (3-v) - 4\pi\gamma_{12} R^2 v \cos \theta \\ & + 2\pi\Delta G_V R^3 \frac{e}{(bc)^{3/2}} \left[ -\frac{e^2 k^2}{3} \sin \varphi \cos \varphi (1-k^2 \sin^2 \varphi)^{\frac{1}{2}} \right. \\ & \left. - \frac{f^2}{3} \{ F(k, \frac{1}{2}\pi) - F(k, \varphi) \} + \left\{ 1 + \frac{2(e^2+f^2)}{3} \right\} \{ E(k, \frac{1}{2}\pi) - E(k, \varphi) \} \right] \\ & + 4\pi\gamma_{12} R^2 \frac{eb}{(cb)^{3/2}} \{ E(k, \frac{1}{2}\pi) - E(k, \varphi) \}. \dots \quad (36) \end{aligned}$$

Case (iii $\beta$ ) :  $a=-c$ , maximum at  $x(v)=0$

$$\begin{aligned} \Delta G = & -\frac{2}{3}\pi\Delta G_V R^3 v^2 (3-v) - 4\pi\gamma_{12} R^2 v \cos \theta \\ & + 2\pi\Delta G_V R^3 \frac{e}{(bc)^{3/2}} \left[ \frac{e^2 k^2}{3} \sin \varphi \cos \varphi (1-k^2 \sin^2 \varphi)^{\frac{1}{2}} \right. \\ & \left. - \frac{f^2}{3} F(k, \varphi) + \left\{ 1 + \frac{2(e^2+f^2)}{3} \right\} E(k, \varphi) \right] \\ & + 4\pi\gamma_{12} R^2 \frac{eb}{(cb)^{3/2}} E(k, \varphi). \dots \quad (37) \end{aligned}$$

Case (iv) :  $\theta_c=0$

$$\Delta G = 2\pi\Delta G_V R^3 v \{ u^2 - \frac{1}{3}v(3-v) \} + 4\pi\gamma_{12} R^2 v \{ u - \cos \theta \}. \dots \quad (38)$$

Case (v) :  $b=\infty$

$$\begin{aligned} \Delta G = & \frac{2}{3}\pi\Delta G_V R^3 \left\{ \frac{2}{c^3} - \left( 2 - \frac{1}{c} \right)^2 \left( \frac{3}{c} - 2 + v \right) - v^2 (3-v) \right\} \\ & + 4\pi\gamma_{12} R^2 \left\{ \frac{1}{c^2} - \frac{1}{c} (2-v) - v \cos \theta \right\}. \dots \quad (39) \end{aligned}$$

These equations may all be written in the form

$$\Delta G = \Delta G_V R^3 E + R^2 F. \dots \quad (40)$$

The values of  $E$  and  $F$  were tabulated for the values of  $a$  and  $c$  shown in Figure 5.

\* The subscript  $i$  in  $v_i$  is dropped beyond this point.

(c) Calculation of Relation between  $R$  and Supersaturation

It is usual to calculate the supersaturation at which the rate of nucleation becomes appreciable. For a spherical particle the rate, per particle, is

$$J = 4\pi 10^{25} R^2 \exp(-\Delta G^*/kT), \quad \dots \dots \dots (41)$$

where  $\Delta G^*$  is the free energy of the critical embryo. The pre-exponential term is only known to within a factor of 100, but this is relatively unimportant as the rate increases very rapidly when the free energy of the embryo is in the neighbourhood of  $\Delta G^*$ . It will be clear from the curves which follow that the critical supersaturation may be readily obtained graphically without direct recourse to an equation of the type of (41) which requires  $\Delta G^* \simeq 60kT$  to satisfy it (Fletcher 1960).

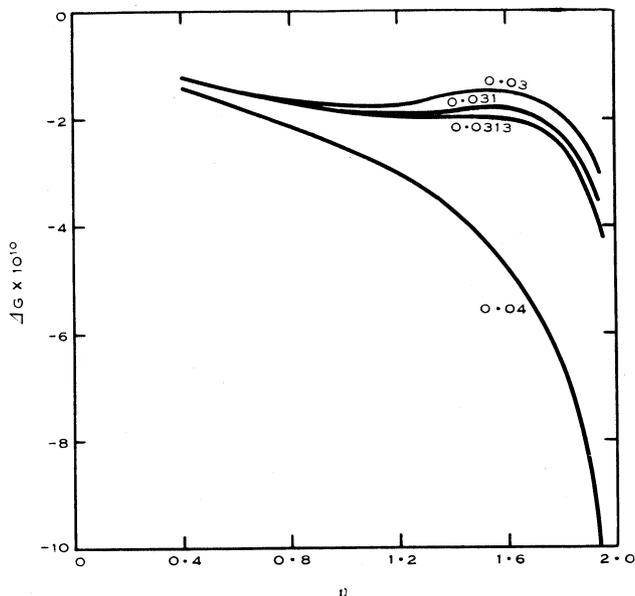


Fig. 6.—The variation in free energy of a liquid embryo with size. The ordinate gives the point of intersection of the generating curves (see Fig. 4).  $R = 10^{-6}$  cm;  $\theta = 10^\circ$ ; temperature  $0^\circ\text{C}$ ; the curves are labelled with the values of  $\log_{10} P/P_s$ , the value 0.0313 being critical.

(i) *Condensation*.—If  $P$  is the partial pressure of water vapour in the gas and  $P_s$  that of the saturated vapour at the same temperature, then

$$\Delta G_V = -(RT/V_L) \ln(P/P_s), \quad \dots \dots \dots (42)$$

where  $V_L$  is the molar volume of water,  $R$  the gas constant, and  $T$  the absolute temperature. We shall adopt the same values as did Fletcher for  $\gamma_{12} = 75.6$  erg  $\text{cm}^{-2}$  at  $0^\circ\text{C}$ . Using  $\theta = 10^\circ$ , the variation of  $\Delta G$ , at a given radius for a monomer particle, is calculated as a function of  $v$ , i.e. as the embryo increases in volume the meniscus will move around the sphere. Figure 6 shows the curves obtained at four different supersaturations. At  $\log_{10} P/P_s = 0.04$  the embryo grows

spontaneously even from the smallest size. At 0.03 a hump has appeared in the curve and at this supersaturation the difference in free energy between the minimum (spontaneous capillary condensation) and the maximum is so large that the nucleation rate is infinitesimally small. A free energy barrier (the hump in the curve) for the required nucleation rate is  $2 \times 10^{-12}$  ergs per embryo, so that for an appreciable rate of nucleation only a plateau will be apparent, on the scale shown. This is found at  $\log_{10} P/P_s = 0.0313$  for dimers of particle radius  $10^{-6}$  cm.

Figure 7 compares the variation of  $P/P_s$  with the radii of the particles forming a dimer to that for monomer particles. It is only for particle radii between  $10^{-6}$  and  $10^{-7}$  cm that appreciable differences appear.

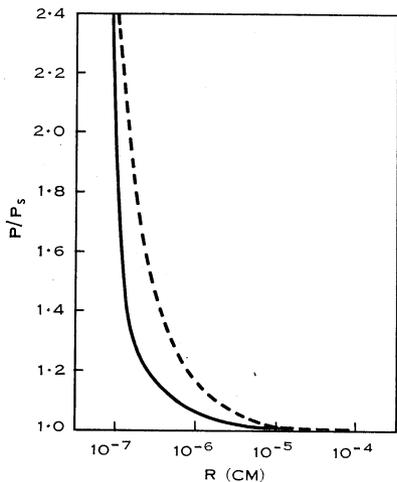


Fig. 7

Fig. 7.—The supersaturation,  $P/P_s$ , at which water condenses on a dimer consisting of particles of radius  $R$ . Temperature  $0^\circ\text{C}$ ; contact angle  $10^\circ$ . The broken curve is for a monomer of radius  $R$ .

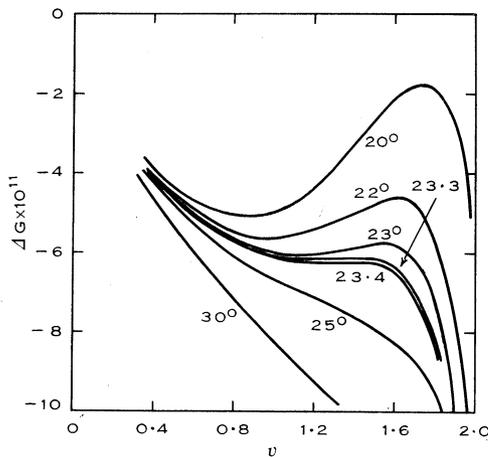


Fig. 8

Fig. 8.—The variation in free energy with size of embryos formed by sublimation at different supersaturations;  $R = 10^{-6}$  cm;  $\theta = 10^\circ$ ; curves are labelled with the values of  $\Delta T$  (the supercooling), the value  $23.4^\circ\text{C}$  being critical.

(ii) *Sublimation.*—The motive free energy is given by

$$\Delta G_V = -(RT/V_s) \ln (P_L/P_I), \quad \dots \dots \dots (43)$$

where  $V_s$  is the molar volume of ice,  $P_L$  is the vapour pressure of a flat water surface, and  $P_I$  that of a flat ice surface. Again, as treated by Fletcher (1958), we shall neglect effects of disregistry and lattice strain except insofar as these are included in the contact angle relating the surface free energies. The vapour pressure  $P_L$  may be related to the supercooling ( $\Delta T = 273 - T^\circ$ ) necessary for nucleation by

$$\log_{10} (P_L/P_I) = \alpha \Delta T, \quad \dots \dots \dots (44)$$

where  $\alpha = 0.00972/\text{degC}$ . A value of  $100 \text{ erg cm}^{-2}$  (Fletcher 1958) is assumed for  $\gamma_{12}$ . Figure 8 shows the variation in free energy for the growth of an embryo on a dimer consisting of particles of  $10^{-6}$  cm radius. Figure 9 compares the

supercooling required for different radii of monomer and dimer. It is apparent that the disability conferred on a particle by a finite contact angle is removed by the formation of dimers. There is, in principle, a considerable gain in the use of dimers formed by spheres in the useful range ( $10^{-6}$  to  $10^{-5}$  cm) of sizes where a number of particles can be produced per unit weight of seeding material.

(iii) *Freezing*.—A similar calculation to that for sublimation is made for the process of nucleation by a dimer suspended in supercooled water. Here the  $\gamma_{12}$  value for the ice-water interface is taken as  $20 \text{ erg cm}^{-2}$  (Fletcher 1958) and the results are shown in Figure 10. Again there appears to be considerable advantage in the use of dimers or polymers.

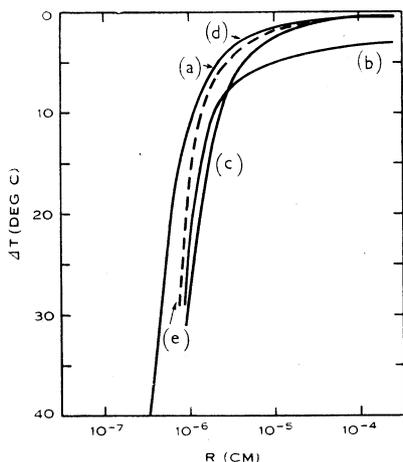


Fig. 9

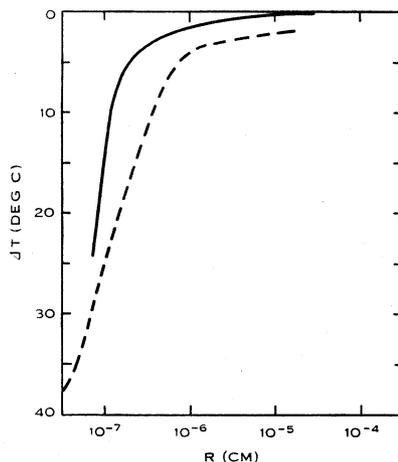


Fig. 10

Fig. 9.—The supercooling  $\Delta T$  at which ice is formed by sublimation on: (a) a dimer consisting of spherical particles of radius  $R$ ; (b) a monomer (spherical particles) of radius  $R$ ; (c) a ledge of width and height  $l$ , and length  $l$ ; (d) a ledge of width and height  $l$ , and length  $5l$ ; (curves (a) and (d) are superimposed). Contact angle  $10^\circ$  for (a), (b), (c), (d). (e) A monomer (spherical particles) of radius  $R$  but contact angle  $0^\circ$ .

Fig. 10.—The supercooling  $\Delta T$  at which ice is formed by freezing on a dimer consisting of particles of radius  $R$ . Contact angle  $10^\circ$ . The broken curve is for a monomer of radius  $R$ .

## V. PROPERTIES OF A LEDGE FORMED BY PLATE DIMERS

If the aerosol of silver iodide is formed by evaporation, the particles are usually crystalline hexagonal plates. Suppose that a dimer forms by one plate lying partially over another. For simplicity consider a ledge, such as that shown in Figure 1 (b), in which the height and width are equal to  $l$  and its length is  $nl$ . For the calculation  $n$  will be chosen as 1 and 5.

It will be assumed that the embryo is contained by a cylindrical surface and having two ends cut square. This form of surface will *not* be that giving the minimum free surface energy and consequently the dimers will be more effective than we calculate. At undersaturations the embryo lies within the step and if the contact angle is greater than  $\frac{1}{4}\pi$ , Wylie (1952) has shown that it rests in the ledge as a segment of a sphere. At or near saturation the embryo meets the

ledge edges  $A, B$  and during further growth the contact angle  $\theta$  is indeterminate until the embryo forms the angle  $\theta$  with the surfaces outside the ledges, when it may again move over the surface.

As long as the centres of the circles forming the embryo surface lie below  $AB$ , the curvature is convex, and the embryo is constrained between  $AB$ , the free surface energy is given by

$$\begin{aligned} \Delta G = & \Delta G_v \omega \left\{ \rho^2 \arcsin \frac{l}{(\sqrt{2})\rho} + \frac{1}{2}l^2 - \frac{1}{2}(2\rho^2 - l^2)^{\frac{1}{2}} \right\} \\ & + 2\gamma_{12} \left\{ \omega \left( \arcsin \frac{l}{(\sqrt{2})\rho} - l \cos \theta \right) + \rho^2 \arcsin \frac{l}{(\sqrt{2})\rho} \right. \\ & \left. - \frac{1}{2}(2\rho^2 - l^2)^{\frac{1}{2}} + \frac{1}{2}l^2 \right\}, \dots\dots\dots (45) \end{aligned}$$

where  $\omega$ , the length of the embryo, is less than or equal to  $nl$  and  $\rho$  is the radius of the surface. For the cylindrical surface taken, it may be shown that, provided the contact angle is less than  $34^\circ$ , the embryo fills the whole length of the ledge, i.e.  $\omega = nl$ , even at the maximum curvature of the surface. For surfaces of small curvature, like the flat surface joining  $AB$ , the contact angle may be as high as  $\frac{1}{2}\pi$  before the embryo segments.

(a) *Calculation of the Relation between Size of Ledge and Nucleation*

Calculations were confined to sublimation nuclei using the constants of Section IV (c) (ii) and a value of  $n=1$  and 5. The most rapid process was to plot the variations of  $\Delta G$  with the volume of the embryo (the term attached to  $\Delta G_v$  in equation (45)). The curves are similar in shape to Figure 8; Figure 9 shows the variation of supercooling with step height and length. The dimer forming a ledge, of height and width  $l$ , is not as effective as a dimer formed from spheres of radius  $R$  but most of this difference will arise from the choice of a free surface energy which is not minimal (see preceding section). The dimer formed with step lengths of  $5l$  are apparently more effective but to form a step of length  $5l$  the particles must have dimensions of at least  $5l$  by  $l$  by  $l$  or more probably  $5l$  by  $5l$  by  $l$ , i.e. to the equivalents of particles of  $1.71R$  and  $2.92R$  respectively. Plotting the curve for the ledge dimer  $5l$  using either of these values of  $R$  practically superimposes it on the ledge curve for a step  $l$ , i.e. the activity at a given ledge height per unit volume of dimer is constant. It is likely that ledge dimers of all sizes are as effective as dimers formed from spheres. It is certain that ledges are advantageous when the particles are large, for then the effect of a finite contact angle is almost removed.

VI. CONCLUSIONS

An aerosol allowed to aggregate will show a decrease in the total number of active particles but with an increasing proportion of particles active at higher temperatures. Where point contacts or ledges form (and, by inference, corners) these are likely to be very active in two senses. They generally raise the temperature at which nucleation is possible on a given substrate. This is of

considerable importance since the number of natural clouds at temperatures close to  $0^{\circ}\text{C}$  exceeds those at the more usual temperature ( $-10^{\circ}\text{C}$ ) where nucleation with silver iodide is effective. For a given mass of silver iodide it might well be more effective to dispense slightly coagulated smokes. If the particles in the smokes are tabular there may not be any advantage in coagulation, except for very coarse smokes, which are probably uneconomic in application anyway. Methods of producing monodisperse aerosols are being studied so that the various models may be differentiated.

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