QUARTERLY REVIEWS

NUCLEATION IN PHASE CHANGES

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List of Symbols

$\alpha = p/p_\infty$
γ = Surface free energy per molecule
δ = Critical supercooling
ε = Edge free energy per cm.
η = ,, ,, ,, ,, molecule
θ = Contact angle
λ_f, λ_s, λ_v = Heats of fusion, solution, and vaporisation, per mole.
ν = Vibration frequency
$\xi = n - n_c$
ρ = Density
ρ', ρ_c' = Radius and critical radius of two-dimensional nucleus
σ, σ_s, σ_l, σ_{sl}, σ_{sv} = Interfacial free energy per cm.^{2} for general surface, solid–vacuum, liquid–vapour, solid–liquid, and solid–vapour interface
$\phi(n)$ See equation (25)
ϕ = Strain energy per molecule
$A = 32\sigma^3 M^2 T_m^2/(k\rho^2\lambda_f^2)$
A_1 = Activation energy for desorption, per molecule
a = Lattice spacing
$a(n)$ = Rate of condensation in mols. per sec. on a nucleus of n molecules
$B = E_D/k$
C = Collision frequency for two dimensions
c_1, c_1', c_x = Surface concentration when $\alpha = 1$, in equilibrium with curved edge, and when $p/p_\infty = \alpha$, respectively
D = Effective dielectric constant
E_D = Activation energy for bulk diffusion, per molecule
E_s, E_l = Energy of mol. of liquid due to solid and liquid sphere
e = Charge on ion on a drop
f = Factor such that number of mols. in surface of nucleus of n mols. is $fn^{2/3}$
g = Factor such that number of mols. in edge of two-dimensional nucleus of n mols. is $gn^{1/2}$
$\Delta G(n)$, $\Delta G_{\text{max.}}$, ΔG_a, ΔG_v = Gibbs free energy of formation and maximum

thereof of nucleus from supersaturated vapour or other phase, free energy of formation of nucleus, per atom and per c.c. of new phase, respectively

$\boldsymbol{h}$ = Planck's constant

h_1 = Height of cylindrical cavity

$I(n)$ = Net rate of formation of nuclei of n mols., per c.c. per sec., from nuclei containing $(n - 1)$ molecules

$\boldsymbol{k}$ = Boltzmann's constant

k_0 and k_1 = Frequency and shape factors [cf. equations (48) and (55), respectively]

l_1, l_c = Edge length of cubic nucleus and of critical cubic nucleus

L_c = Edge length of critical square nucleus

M = Molecular weight

m = Number of moles

N = Large number—cf. equation (31)

N_{A} = Avogadro's number

n, n_c = Number of molecules in nucleus and critical nucleus

n_s = Number of atoms in melt per cm.^{2}

n_1 = Number of molecules per c.c. in the melt

p, p_∞ = Supersaturated and saturated vapour pressure

$q(n)$ = Rate of evaporation of nucleus of n mols., in mols. per sec.

r = Radius of nucleus or of cylindrical cavity

$\boldsymbol{R}$ = Gas constant per mole

$s(n)$ = Number of mols. in the surface of a nucleus of n mols.

S, S_∞ = Saturated and supersaturated solubility

T_0, T_m, T_s, T_c, T = Temperature (in ° K.) from which cooling occurred, m.p., temp. of saturation, critical temp. for separation of alloy, and temp., respectively

$U(n)$ = Energy of nucleus of n mols.

U_D = Activation energy for diffusion in two dimensions, per molecule

$V = V_{\mathrm{AB}} - \frac{1}{2}(V_{\mathrm{AA}} + V_{\mathrm{BB}})$; V_{AA} etc. = bond energies

$v(\rho)$, $v(\infty)$ = Growth rate of curved and straight edge

x = Mole-fraction

X, Y = Constants ; cf. equation (60)

$Z(n)$ = Number of nuclei of n molecules per cm.^{3}

z = Co-ordination number

WHEN one phase is changed into another the new phase, although thermodynamically stable, appears in general in the form of nuclei only when a considerable supersaturation or supercooling has been achieved. The theory of the process combines kinetics and thermodynamics in an interesting way, and has recently attracted considerable attention.[1] The present Review

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[1] General references : Volmer, " Kinetik der Phasenbildung ", Steinkopff, Dresden and Leipzig, 1939 ; Frenkel, " Kinetic Theory of Liquids ", Oxford, 1946, Chap. VII ; Straumanis, " Heterogene Katalyse ", I, Springer-Verlag, Vienna, 1943, p. 269 ;

is not intended to be exhaustive but rather to show, in the light of recent views, the interrelation of many diverse fields.

Section I. Three-dimensional nucleation

The Thermodynamics of Nucleus Formation from the Vapour Phase.—If A and B are two phases, such that A is unstable with respect to B when A and B are in bulk, it is possible for nuclei of B to be in equilibrium with A, since the decrease in Gibbs free energy in transferring dm moles from A to B is offset by the increase in surface free energy of the whole nucleus. A spherical nucleus of radius r formed in a vapour of pressure p will be in equilibrium if Kelvin's relation is obeyed, *i.e.*, if

$$RT \log (p/p_\infty) = 2\sigma M/(r\rho) \quad . \quad . \quad . \quad (1)$$

where p_∞ is the vapour pressure over a plane surface, σ is the surface free energy per cm.^{2}, M the molecular weight, and ρ the density. As will be shown below, the equilibrium is an unstable one.

The corresponding equation for a cubic crystal of edge l may be found by equating (a) the Gibbs free energy of transfer of dm moles from an infinitely large crystal to the crystal nucleus with (b) the gain in free energy due to increase in size of the nucleus. If we write

$$p/p_\infty = \alpha$$

this gives
$$\mathrm{d}m . RT \log \alpha = \sigma \mathrm{d}(6l^2) = 12\sigma l . \mathrm{d}l \quad . \quad . \quad . \quad (2)$$

Since
$$\mathrm{d}m = \mathrm{d}(l^3)\rho/M = 3l^2\rho . \mathrm{d}l/M$$

we obtain
$$RT \log \alpha = 4\sigma M/(l\rho) \quad . \quad . \quad . \quad . \quad (3)$$

This treatment neglects the edge energy, ε ergs per cm. If this is included, equation (2) becomes

$$\mathrm{d}m . RT \log \alpha = 12\sigma l . \mathrm{d}l + 12\varepsilon . \mathrm{d}l$$

giving
$$RT \log \alpha = 4\sigma M/(l\rho) + 4\varepsilon M/(l^2\rho) \quad . \quad . \quad (4)$$

Equations (1), (3), and (4) refer to equilibrium nuclei. The Gibbs free energy of formation from the vapour of a spherical nucleus of any radius r may be written as the sum of a bulk and a surface term, or

$$\Delta G = -\frac{4}{3}\pi r^3 \frac{\rho}{M} RT \log \alpha + 4\pi r^2 \sigma \quad . \quad . \quad . \quad (5)$$

ΔG, when plotted as a function of r, passes through a maximum, as seen in Fig. 1, which gives the free energy of formation of water drops from water vapour with $\alpha = 4$ at 0° C. When

$$\mathrm{d}(\Delta G)/\mathrm{d}r = 0, \quad RT \log \alpha = 2\sigma M/(r\rho) \quad . \quad . \quad (6)$$

which is, of course, the equilibrium condition. Equation (6) may be interpreted as giving the radius r_c of the so-called critical nucleus for which ΔG is a maximum for a given value of p, or equally well as giving the vapour pressure p in equilibrium with any radius r. Since $\mathrm{d}^2(\Delta G)/\mathrm{d}r^2$ is negative, as is evident from equation (5) and from the graph, the equilibrium is

Discuss. Faraday Soc., " Crystal Growth ", 1949, No. 5 ; Buckley, " Crystal Growth ", Wiley, New York, 1951 ; Wells, *Ann. Reports*, 1946, **43**, 62 (cf. p. 85).

unstable. The critical nucleus corresponding to the conditions applying to Fig. 1 contains about 90 molecules. Nuclei of radii less than the critical radius may be described as embryonic.

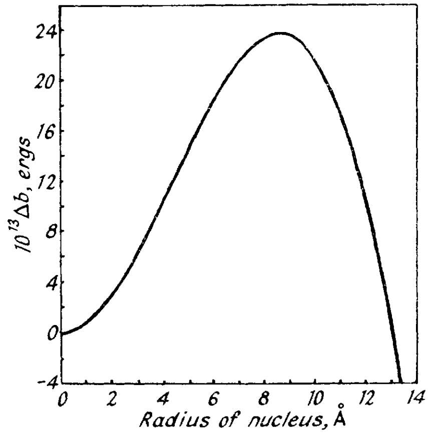

FIG. 1

If we combine equations (6) (with $r = r_c$) and (5), we obtain

$$\Delta G = -\,8\pi r^3\sigma/(3r_c) + 4\pi r^2\sigma = 4\pi r^2\sigma[1 - 2r/(3r_c)] \quad . \qquad (7)$$

and $$\Delta G_{\text{max.}} = 4\pi r_c^2\sigma/3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

Hence the free energy of formation of the critical nucleus is one-third of the surface free energy of the whole drop. Similarly, for the cubical nucleus of edge l,

$$\begin{aligned}\Delta G &= -\,l^3\rho\frac{RT}{M}\log\alpha + 6\sigma l^2 + 12l\varepsilon \quad . \quad . \quad . \quad . \qquad (9)\\ &= -\,l^3 4\sigma/l_c - l^3 4\varepsilon/l_c^2 + 6\sigma l^2 + 12l\varepsilon\\ &= 6\sigma l^2[1 - 2l/(3l_c)] + 12l\varepsilon[1 - l^2/(3l_c^2)]\end{aligned}$$

Hence $$\Delta G_{\text{max.}} = 6\sigma l_c^2/3 + 8\varepsilon l_c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

The simple relation, $\Delta G_{\text{max.}} = \frac{1}{3}$ (the surface free energy of the whole nucleus), which Gibbs [2] considered to be general, is true for crystals only if the edge energy, which may be important for small crystals, is neglected.

These interesting relations may be written in other forms ; for example, r_c may be eliminated from equation (8), with the following result :

$$\Delta G_{\text{max.}} = 16\pi\sigma^3 M^2/[3\rho^2(RT\log\alpha)^2] \quad . \quad . \quad . \quad . \qquad (11)$$

Moreover, it is often convenient to express these relations in terms of the surface free energy per molecule (γ) rather than in that per cm.^{2} (σ), and in terms of the number of molecules (n) in the nucleus rather than of the radius (r). If we omit the consideration of edge energies and of crystals with faces of different values of σ, we obtain as a general expression for

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[2] " Scientific Papers ", Longmans, 1906, p. 322.

the free energy of formation $\Delta G(n)$ of a nucleus containing n molecules from vapour at pressure p

$$\Delta G(n) = -nkT\log\alpha + f\gamma n^{2/3} \quad . \quad . \quad . \quad (12)$$

where f is a geometrical factor such that the number of molecules in the whole surface is $fn^{2/3}$. When

$$d[\Delta G(n)]/dn = 0, \quad -kT\log\alpha + 2f\gamma/(3n^{1/3}) = 0,$$

or

$$n_c^{1/3} = 2f\gamma/[3kT\log\alpha] \quad . \quad . \quad . \quad . \quad (13)$$

and

$$\Delta G_{\text{max.}} = f\gamma n_c^{2/3}/3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$= 4(f\gamma)^3/[27(kT\log\alpha)^2] \quad . \quad . \quad . \quad (15)$$

The shape of the curve obtained by plotting ΔG against r when $\alpha > 1$ must be contrasted with that of the continuously rising curve which is obtained when $\alpha < 1$ and when both terms of equations (5) and (12) are positive. Under the latter conditions the theory of fluctuations may properly be applied, and clusters of molecules of the phase B will be present in the unsaturated phase A. Such clusters form and break up in dynamic equilibrium, and the concentration of clusters of size corresponding to a free energy of formation ΔG will be proportional to exp. $[-\Delta G/(kT)]$, so that clusters of any appreciable size will be extremely rare. In contrast, when $\alpha > 1$, or $p > p_\infty$, ΔG decreases to zero after passing through a maximum, and then becomes negative, so that a slight displacement beyond the equilibrium position causes the precipitation of the phase B in bulk. Fluctuation theory may be applied to the rising part of the ΔG–r curve when $\alpha > 1$, and indeed the embryonic nuclei must be formed by such fluctuations. According to fluctuation theory the embryonic nuclei will be more populous the lower the value of ΔG, whereas, according to thermodynamics, they will have a higher equilibrium vapour pressure the lower the value of ΔG and would be less likely to form. We may regard the embryonic nuclei as forming and breaking up continuously, until they reach the critical size, when a favourable fluctuation will cause them to grow indefinitely. The critical free energy of formation thus plays the part of a free energy of activation.

The remarks above apply to the nuclei in equilibrium with vapour of various degrees of supersaturation at constant temperature. It is also possible to cause supersaturation by maintaining the molar concentration of vapour at a constant value by cooling from T_0, when the vapour is saturated at vapour pressure p, to T, when the saturated vapour pressure is p_∞, and $\alpha = p/p_\infty$ if no allowance is made for the change of pressure p with temperature at constant volume. Since

$$\log(p/p_\infty) = \frac{\lambda_v}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

approximately, where λ_v is the latent heat of vaporisation per mole,

$$RT\frac{\lambda_v}{R}\cdot\frac{T_0 - T}{TT_0} = \frac{2\sigma M}{r\rho}, \quad \text{or} \quad T_0 - T = 2\sigma MT_0/(r\rho) \quad . \quad (16)$$

Equation (16) gives the value of r for the equilibrium nucleus at T.

Some doubt may be felt about the application of Kelvin's equation to nuclei, since it is impossible to differentiate surface and bulk molecules with, for instance, a cube of eight molecules, and at the lower limit embryonic nuclei pass into dimers and trimers. However, it would be possible to restate the relations in terms of a real quantity, *viz.*, the mean evaporation energy per molecule; moreover, the critical nucleus frequently contains roughly 100 molecules, and the decrease in surface energy per cm.^{2} for such a nucleus will probably be only of the order of 10%.[3] This value has been confirmed by Benson and Shuttleworth,[3] who find that for a close-packed nucleus containing only 13 molecules the surface energy per cm.^{2} decreases by less than 15% from the value for a large surface. It may be noted that the surface energy per cm.^{2} remains constant down to very small dimensions if the interaction energy is confined to nearest-neighbour interactions. These remarks would require qualification if the critical nucleus consisted of a thin plate.

The Kinetics of Nucleation from the Vapour Phase.—Thermodynamical arguments provide no information on the rate of nucleation, except that a dependence on the concentration of critical nuclei might be expected, so that the rate would be very small for low degrees of supersaturation (α near to 1). The kinetics of nucleation have been developed by Farkas,[4] Volmer,[1] Stranski and Kaischew,[5] and especially by Becker and Döring.[6] The following is a simplified version of the work of Becker and Döring based on, but not identical with, Frenkel's derivation.[1] No rigorous solution of the problem exists and Becker and Döring's treatment is approximate and to some extent unreal. In view of the key position occupied by this theory it is given in some detail, the mathematics being tedious rather than difficult.

The energy $\Delta U(n)$ required to vaporise a nucleus containing n molecules may be written in the form

$$\Delta U(n) = nW - f\gamma n^{2/3} \quad . \quad . \quad . \quad . \quad (17)$$

where W is the heat of vaporisation per molecule, and where for simplicity surface free energies are equated to surface energies. Hence the energy required to transfer dn molecules from one nucleus to the vapour is

$$\begin{aligned} \mathrm{d}\Delta U(n) &= \mathrm{d}n(W - 2f\gamma n^{-1/3}/3) \quad . \quad . \quad . \quad (18) \\ &= \mathrm{d}n\,.\,W(n) \quad . \quad . \quad . \quad . \quad . \quad . \quad (19) \end{aligned}$$

where $W(n) = W - 2f\gamma n^{-1/3}/3$. For simplicity n is assumed to take the values unity upwards, although of course these equations cannot in fact be applied in the region of low values of n.

Let us suppose that nuclei can grow as a result of molecular collisions from the vapour, and that they can also decrease their size by evaporation. Let $q(n)$ and $a(n)$ be respectively the rate of evaporation and condensation

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[3] Bradley, *Trans. Faraday Soc.*, 1940, **36**, 392 (last paragraph); Benson and Shuttleworth, *J. Chem. Physics*, 1951, **19**, 130; Tolman, *ibid.*, 1948, **16**, 758; 1949, **17**, 118, 333; La Mer and Pound, *ibid.*, p. 1337; 1951, **19**, 506.

[4] *Z. physikal. Chem.*, 1927, **125**, 236.

[5] *Ibid.*, 1934, *B*, **26**, 317.

[6] *Ann. Physik*, 1935, **24**, 719.

in molecules per second on a nucleus containing n molecules of which $s(n)$ molecules are in the surface. Then

$$q(n) = s(n)\nu \exp.[- W(n)/(\boldsymbol{k}T)] \quad . \quad . \quad . \quad (20)$$

where ν is the vibration frequency of a surface molecule for vibrations perpendicular to the surface, and the expression for the vacuum rate is used (although most of the work has been done on water vapour in air) because the drops are very small ; for such small drops evaporation is not governed by diffusion.[7] Similarly,

$$a(n) = s(n)\nu\alpha \exp.[- W/(\boldsymbol{k}T)] \quad . \quad . \quad . \quad (21)$$

since at an equilibrium pressure p_∞ the rates of evaporation and condensation are equal for a patch of *plane* surface containing $s(n)$ molecules, so that the rate of condensation is given by $s(n)\nu \exp.[- W/(\boldsymbol{k}T)]$. It follows that at pressure p the rate of condensation on such a patch is given by

$$\frac{p}{p_\infty}s(n)\nu \exp.[- W/(\boldsymbol{k}T)]$$

and this must also be the rate of condensation on the curved surface. It should be noted that expression (20) contains $W(n)$ since this is the activation energy for the loss of a molecule from a nucleus containing n molecules, whereas equation (21) contains W, since the rate of evaporation from a plane surface determines the saturation vapour pressure, which is a function of W.

The actual problem of the formation of nuclei may be replaced by the easier but less real problem of a system of nuclei in a stationary state, *i.e.*, the concentration of nuclei of any size remains constant, so that

$$I(n) = I(n + 1) = I \quad . \quad . \quad . \quad . \quad (22)$$

for all values of n, where $I(n)$ is the net rate of formation per second per cm.^{3} of nuclei containing n molecules, from nuclei containing $(n - 1)$ molecules ;

$$\mathrm{d}Z(n)/\mathrm{d}t = I(n) - I(n + 1) = 0$$

for the stationary state, where $Z(n)$ is the concentration per cm.^{3} of nuclei containing n molecules.

In order to keep up the steady flow of nuclei it will be necessary to remove those nuclei which have grown well past the critical size, say those containing N molecules, and replace them by an equivalent quantity of vapour. As will be seen later, the choice of N is immaterial. It follows that

$$I(n) = Z(n - 1)a(n - 1) - Z(n)q(n) \quad . \quad . \quad (23)$$

Similarly, $$I(n + 1) = Z(n)a(n) - Z(n + 1)q(n + 1) \quad . \quad . \quad (24)$$

The mathematical argument is simplified if we now *define* a function $\phi(n)$ by the relation

$$\begin{aligned} a(n)\phi(n) &= Z(1)a(1)\alpha^n \exp.[-f\gamma n^{2/3}/(\boldsymbol{k}T)] \\ &= Z(1)a(1) \exp.[- \Delta G(n)/(\boldsymbol{k}T)] \quad . \quad . \quad (25) \end{aligned}$$

from equation (12). Then

$$q(n)\phi(n) = Z(1)a(1)\alpha^{n-1} \exp.[-f\gamma(n^{2/3} - \tfrac{2}{3}n^{-1/3})/(\boldsymbol{k}T)] \quad . \quad (26)$$

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[7] Bradley, Evans, and Whytlaw-Gray, *Proc. Roy. Soc.*, 1946, *A*, **186**, 368.

since the ratio $a(n)/q(n)$ from equations (20) and (21) is given by

$$a(n)/q(n) = \alpha \exp.[-2f\gamma n^{-1/3}/(3\boldsymbol{k}T)] \qquad (27)$$

Now if n is sufficiently large

$$n^{2/3} - \tfrac{2}{3}n^{-1/3} = n^{2/3}[1 - 2/(3n)]$$

$$= n^{2/3}\left(1 - \frac{1}{n}\right)^{2/3} \text{ (app.)}$$

$$= (n-1)^{2/3} \text{ (app.)}$$

Hence

$$q(n)\phi(n) = a(n-1)\phi(n-1) \text{ (app.)} \qquad (28)$$

It follows from equation (23), by eliminating $q(n)$ (by using 28), that

$$I/[a(n-1)\phi(n-1)] = Z(n-1)/\phi(n-1) - Z(n)/\phi(n) \qquad (29)$$

$$= -\mathrm{d}[Z(n)/\phi(n)]/\mathrm{d}n \qquad (30)$$

if dn is equated to 1 (one molecule). Hence

$$I\int_1^N \mathrm{d}n/[a(n-1)\phi(n-1)] = -[Z(n)/\phi(n)]_1^N \qquad (31)$$

since I is a constant independent of n.

Now $Z(N)$ is by definition zero, since nuclei of this size are removed, and $\phi(1) = Z(1)\exp.[-\Delta G(1)/(\boldsymbol{k}T)] = Z(1)$, since no energy is needed to form a nucleus of one molecule from single molecules! Hence

$$I\int_1^N \mathrm{d}n/[a(n-1)\phi(n-1)] = 1$$

and

$$I = Z(1)a(1)/\int_1^N \exp.[\Delta G(n)/(\boldsymbol{k}T)] \qquad (32)$$

equation (25) being used and $n - 1$ replaced by n, as an approximation.

Since $\Delta G(n)$ has a maximum at $n = n_c$, $\exp.[\Delta G(n)/(\boldsymbol{k}T)]$ will have a very sharp maximum at this point, and it suffices to replace $\Delta G(n)$ by the first two terms of the Taylor series

$$\Delta G(n) = \Delta G(n_c) + \tfrac{1}{2}\xi^2\left[\frac{\mathrm{d}^2\,\Delta G(n)}{\mathrm{d}\xi^2}\right]_{n=n_c}$$

where for convenience the origin has been transferred to $n = n_c$ and where $\xi = n - n_c$. Now

$$[\mathrm{d}^2\,\Delta G(n)/\mathrm{d}\xi^2]_{\xi=0} = -2f\gamma n_c^{-4/3}/9 \qquad (33)$$

from (12). Hence

$$\int_1^N \exp.[\Delta G(n)/(\boldsymbol{k}T)]\mathrm{d}n$$

$$= \exp.[\Delta G(n_c)/(\boldsymbol{k}T)]\int_{-\infty}^{\infty} \exp.[-\xi^2 f\gamma n_c^{-4/3}/(9\boldsymbol{k}T)]\mathrm{d}\xi \text{ (app.)} \qquad (34)$$

$$= [9\pi\boldsymbol{k}Tn_c^{4/3}/(f\gamma)]^{1/2}\exp.[\Delta G(n_c)/(\boldsymbol{k}T)] \text{ (app.)} \qquad (35)$$

where the limits $\pm\,\infty$ are permitted owing to the sharpness of the maximum ;

it follows that the precise value of N is immaterial. Hence

$$I = Z(1)a(1)[f\gamma/(9\pi \boldsymbol{k}Tn_c^{4/3})]^{1/2} \exp.[-\Delta G_{\text{max.}}/(\boldsymbol{k}T)] \quad . \quad . \quad (36)$$

$$= \frac{Z(1)a(1)}{n_c}[\Delta G_{\text{max.}}/(3\pi \boldsymbol{k}T)]^{1/2} \exp.\left[-\frac{4}{27}\left(\frac{f\gamma}{\boldsymbol{R}T}\right)^3 \frac{1}{(\log \alpha)^2}\right] \quad . \quad (37)$$

which is Becker and Döring's equation.

For $Z(1)a(1)$ we can write the well-known expression for the collision frequency per cm.^{3} per second between single molecules. It is hardly necessary to emphasise that equation (37) is not exact. It will be noted that the so-called nuclear current I is very sensitive to the value of α, so that, although nucleation proceeds at any value of $\alpha > 1$, geological times would be needed to obtain a visible nucleation unless α reaches a quasi-critical value, in agreement with experimental observation on the Wilson cloud chamber.

There is also good numerical agreement with the experimental results of Volmer and Flood [8] on adiabatic expansion of air containing water vapour in absence of ions. Experimentally, α is 5·03 for the condensation of cloud at 261° K. (quoted by Becker and Döring), and when $\log_e I = 1$, *i.e.*, when 2·7 nuclei are formed per second per cm.^{3}, Becker and Döring showed that $\alpha = 5{\cdot}14$ at this temperature. For slightly greater values of α, I would be very large; for slightly smaller values, I would be very small. The more recent work of Sander and Damköhler [9] on purified air containing water vapour free from ions showed that the critical supersaturation pressure down to $-62°$ C. for $I = 1$ is given by

$$\log_e \alpha = 780/T - 1{\cdot}521 \quad . \quad . \quad . \quad (38)$$

and this equation is in reasonable agreement with the predictions of the theory of Becker and Döring (who require, however, a dependence of $\log \alpha$ on $T^{-3/2}$ if I is constant and if the pre-exponential factor is regarded as roughly temperature-independent). Good agreement could be obtained by Sander and Damköhler with an equation they propose, containing an exponential term

$$\exp.[-\Delta G_{\text{max.}}(1 - 4n_c^{-2/3} + 2n_c^{-1})/(\boldsymbol{k}T)]$$

but only if the surface energy of water per cm.^{2} was assumed to be less than the value calculated by linear extrapolation from higher temperatures. It would be of interest to confirm this non-linear dependence of surface energy and temperature for supercooled water, and it is possible that Sander and Damköhler's results could be explained by the fact that the size of the critical nucleus has become very small at large values of α and hence the variation of σ with r should be considered (cf. also La Mer and Pound,[3] 1951). As shown by Flood and Tronstad,[10] heavy water requires a slightly lower adiabatic expansion for critical saturation than light water.

The Law of Stages.—Becker and Döring [6] deduced an expression for the rate of formation of crystalline nuclei including terms to allow for linear and surface nucleation, but these are unnecessary in the case of real crystals,

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[8] *Z. physikal. Chem.*, 1934, *A*, **170**, 273.

[9] *Naturwiss.*, 1943, **31**, 460.

[10] *Z. physikal. Chem.*, 1936, *A*, **175**, 347.

as will be seen later, and will not be discussed. As Becker and Döring point out, these terms have very little influence on the value of α necessary for the onset of visible nucleation, and so long as this is all that is required we may write

$$I_{\text{crystal}} = 2(\text{collision frequency})[\Delta G_{\text{max.}}/(kT)]\ \text{exp.}[-\ \Delta G_{\text{max.}}/(kT)] \quad . \quad (39)$$

The value of I is so sensitive to the value of α that a further simplification is possible if all that is required is an indication of the onset of nucleation, *viz.*

$$I_{\text{liquid or crystal}} = (\text{collision frequency})\ \text{exp.}[-\ \Delta G_{\text{max.}}/(kT)] \quad . \quad (40)$$

It is of interest in this connection to compare the relative probability of the precipitation of the liquid and solid from the vapour. For a cube $f = 6$, whereas for a spherical drop $f = (36\pi)^{1/3}$. If we assume that the molecular volume and surface energy per cm.^{2} are equal in the liquid and the solid state, then equal velocity of nucleation for the production of liquid and cubical solid nuclei occurs when

$$\frac{\log\,(p/p_{\infty\text{s.}})}{\log\,(p/p_{\infty\text{l.}})} = \left(\frac{6^3}{36\pi}\right)^{1/2} = 1{\cdot}38 \quad . \quad . \quad . \quad (41)$$

or

$$\log p = 3{\cdot}6 \log p_{\infty\text{l.}} - 2{\cdot}6 \log p_{\infty\text{s.}} \quad . \quad . \quad . \quad (42)$$

where $p_{\infty\text{l.}}$ and $p_{\infty\text{s.}}$ are the saturation vapour pressures of liquid and solid respectively. Equation (42) gives the value of p, at any temperature, at which the probabilities of forming the solid and liquid nuclei are equal, and is plotted as the line OC in Fig. 2, where O is the melting point. If p is greater than the value given by equation (42), then liquid drops are deposited preferentially. We are, however, interested only in those values of p which give an observable nucleation rate, *i.e.*, the values of p given by the curve DE. At temperatures above C, the meeting point of OC and DE, liquid will be precipitated, whereas below C solid nuclei will be formed directly from the vapour, and not *via* the liquid phase. This shows that Ostwald's rule of stages, according to which the least stable form is the first to precipitate, is not always true even in the absence of adventitious factors such as foreign nuclei.

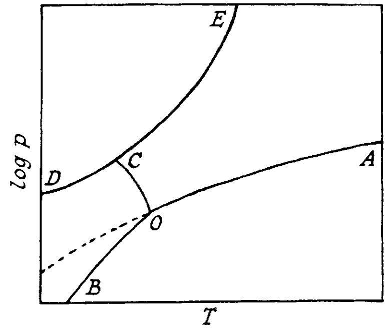

FIG. 2

These expectations have been confirmed by Sander and Damköhler for water vapour in air, since supersaturation above $-$ 62° resulted in the appearance of liquid drops, whereas below $-$ 62° solid was precipitated, as was revealed by the twinkling of the crystals. It was probable that the solid was formed directly, since the presence of ions did not affect the results below $-$ 62°, in contrast to the behaviour above (see the next section). Below $-$ 62° the critical supersaturation was given by

$$\log_e \alpha = 1373/T - 3{\cdot}748$$

in reasonable agreement with Becker and Döring's equation if a surface energy per cm.^{2} of 68—72 ergs per cm.^{2} were postulated for ice ; a small temperature coefficient for σ was assumed. Other workers have found rather higher temperatures for the temperature corresponding to the point C (Fig. 2), possibly because of the presence of foreign particles ; Schaefer,[11] by introducing a cold object into an unpurified cloud, found $-39°$. Cwilong,[12] using air purified by repeated expansion, found a temperature of $-35°$; ice could be detected in the cloud by its inoculating action on supercooled water in the bottom of the cloud chamber. Cwilong remarks, however, that it is easy to obtain water drops at $-50°$.

Cwilong's method for the detection of solid had previously been used by Tammann,[13] who states that cooled vapour of benzophenone gives no inoculation of the melt between 0° and 40° (m.p. 45°).

The Influence of Ions on Nucleation from the Vapour Phase.—Deposition in the Wilson cloud chamber occurs at lower supersaturations in the presence of ions, especially negative ions. J. J. Thomson's original theory [14] gave for the free energy of formation of the drop, which was regarded as a charged conductor,

$$\Delta G = -\frac{4}{3}\cdot\frac{\pi r^3}{M}\rho \log \alpha + 4\pi r^2\sigma + \frac{e^2}{2r} \quad . \quad . \quad . \quad (43)$$

where e is the charge on a drop. ΔG will be a maximum when

$$\frac{\rho}{M}RT \log \alpha = \frac{2\sigma}{r_c} - \frac{e^2}{8\pi r_c^4} \quad . \quad . \quad . \quad . \quad (44)$$

It is, however, unreal to consider a drop which contains one or two ions as a charged conductor with a surface density of charge, and as a step towards reality the ion may be supposed placed at the drop centre, giving

$$\Delta G = -\frac{4}{3}\pi r^3\frac{\rho}{M}RT \log \alpha + 4\pi r^2\sigma - \frac{e^2}{2b}\left(1 - \frac{1}{D}\right) + \frac{e^2}{2r}\left(1 - \frac{1}{D}\right) \quad . \quad (45)$$

where D is the dielectric constant of water in the drop, a value considerably less than the normal owing to dielectric saturation round the ion, and b is the radius of the ion. On differentiating equation (45) we obtain for the critical nucleus

$$\frac{\rho}{M}RT \log \alpha = \frac{2\sigma}{r_c} - \frac{e^2}{8\pi r_c^4}\left(1 - \frac{1}{D}\right) \quad . \quad . \quad . \quad (46)$$

Since the charge acts as if it conferred a negative surface energy per cm.^{2} of value $\frac{e^2}{16\pi r_c^3}\left(1 - \frac{1}{D}\right)$, it is clear that deposition is favoured on ions. Moreover, equation (46) shows that log p when plotted against r_c rises to

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[11] *Chem. Reviews,* 1949, **44,** 291.

[12] *Nature,* 1945, **155,** 361 ; *Proc. Roy. Soc.,* 1947, *A,* **190,** 137.

[13] " The States of Aggregation ", trans. by Mehl, Constable, 1926.

[14] See J. J. Thomson and G. P. Thomson, " Conduction of Electricity through Gases ", C.U.P., 1928, Vol. I, p. 332.

a maximum at

$$r_{c,\,\text{max.}} = \left[\frac{e^2}{4\pi\sigma}\left(1 - \frac{1}{D}\right)\right]^{1/3} \quad . \quad . \quad (47)$$

This shows that p cannot be increased above the value corresponding to $r_{c,\,\text{max.}}$ without the formation of cloud. This may be contrasted with the state of affairs when there is no charge, when $\log p$ increases indefinitely as r_c decreases. Fig. 3 shows the form of the curves; according to J. J. Thomson allowance should also be made for the variation of σ with r.

J. J. Thomson [14] suggested as an explanation for the greater effectiveness of *negative* ions that the uncharged water drop has a natural surface double layer, with the negative charge on the outside. It seems unlikely to the Reviewer that a very small drop with a central ion would exhibit its natural surface double layer, since the water dipoles will be almost fully oriented by the ion. Equation (45) predicts equal effectiveness for positive and negative ions, on the assumption of a continuous dielectric. The greater effectiveness of negative ions may be due to the asymmetric disposition of the water dipole with respect to the molecular centroid, so that the negative ion has a greater hydration energy than a positive ion of equal radius.[15]

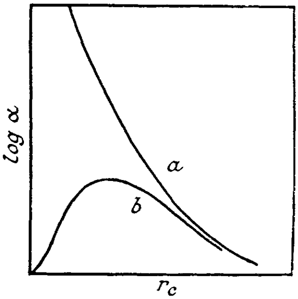

Fig. 3

(*a*) *Without charge.*

(*b*) *Charged drop.*

Loeb and his co-workers [16] found, however, that for condensation from the vapour to give a definite cloud in the cloud chamber, aniline, ethyl iodide, chlorobenzene and toluene also show a negative sign preference, whereas ethyl and methyl alcohol, acetic acid, and n-butyl bromide show a positive reference; benzene, nitrobenzene, chloroform, and acetone show no preference. Loeb believes that the embryonic droplets are pseudo-crystalline, with directed intermolecular van der Waals cohesion. If the approaching molecular dipole is suitably oriented by the ion so that it may fit on to the pseudo-crystal, then there will be a sign preference. For water, Loeb considers that the oxygen atoms project outwards from the surface of the pseudo-crystal, and hence negative ions in the drop will orient molecules of water approaching from the vapour so that they may readily condense. For the alcohols, he considers that the carbon chain is outwards so that positive ions will favour condensation relative to negative ions. Loeb also supposed that the embryonic nuclei do not form round the ion but that the ions are picked up by the drops and may then influence growth. These views are to some extent at variance with those of Sander and Damköhler,[9] who explain the fact that there is no ion preference below − 62° for water condensation by the difficulty in building up a dipole atmosphere round an ion in a crystal of ice.

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[15] Bernal and Fowler, *J. Chem. Physics*, 1933, **1**, 515.

[16] Loeb, Kip, and Einarsson, *ibid.*, 1938, **6**, 264.

Nucleation from the Vapour on Foreign Particles.—A cloud may form in the Wilson chamber for low expansion ratios, and after the cloud has been allowed to settle, and after a few repetitions, values of α of the order of 4 are necessary for cloud formation. This is due to the presence in the first expansions of foreign nuclei, direct evidence for which has been given by Linke,[17] using the electron microscope.

With soluble particles, condensation may occur even in under-saturated air, and this is probably the cause of industrial fog. The action of insoluble particles is more obscure. The most obvious explanation is that the size of the particle permits the formation of drops in equilibrium at low supersaturations. This can hardly be a complete theory, for, if it were, the walls of the vessel would act as a condenser, and Bangham and Saweris [18] have shown that supersaturated streams of vapour can impinge on mica without condensation to liquid, although a film thick enough to show faint interference colours can be built up. Immediate condensation occurs on smoked glass. This indicates that molecules in the uppermost layer of a thick film must differ in potential energy from those on the surface of the bulk liquid, since the former are in equilibrium with supersaturated vapour, and it must be concluded that such layers are affected by the solid substrate.

The film of liquid adhering to a solid nucleus will have a vapour pressure depending on the curvature of the surface, the thickness of the film, and the potential energy due to the solid. It would be expected that the latter would depend on the work of adhesion :

$$\sigma_s + \sigma_l - \sigma_{sl} = \sigma_l(1 + \cos\theta) + \sigma_s - \sigma_{sv},$$

where σ_s, σ_l, σ_{sl}, and σ_{sv} are the surface energies per cm.^{2} of the interfaces solid–vacuum, liquid–vapour, solid–liquid, and solid–vapour, respectively, and θ is the contact angle. It would be expected that a film would form if the solid were wetted. Instead, however, of discussing the three effects separately, a more clear-cut formulation results if the energy of a molecule of the liquid in the outer shell is calculated in terms of the attractions of other molecules of liquid and of the solid. When the central portion of a liquid drop is replaced by solid, the energy of a molecule of liquid is changed by $E_s - E_l$ where E_s is the potential energy of the molecule due to solid and E_l that due to liquid in the shaded portion (Fig. 4). These energies may be evaluated for London interactions, which, even with dipolar molecules, constitute a large part of the cohesive energy, but the expressions are cumbersome and will not be given here.[19] It is clear that the influence of the solid is not necessarily favourable for condensation.

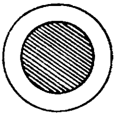

FIG. 4

When the solid is isomorphous with the condensed solid phase, or when the crystalline form is favourable for overgrowths, it is possible for the foreign solid particle to act as a nucleus causing deposition of solid where in its absence liquid drops would be formed. This is observed in the interesting

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[17] *Naturwiss.*, 1943, **31,** 230.

[18] *Trans. Faraday Soc.*, 1938, **34,** 554 ; cf. also Henniker, *Rev. Mod. Physics*, 1949, **21,** 322 ; Bowden and Throssell, *Nature*, 1951, **167,** 601.

[19] See Bradley, *Trans. Faraday Soc.*, 1951, **47,** 630.

experiments of Langmuir[20] and his co-workers on the deposition of ice on a smoke of finely divided silver iodide, which causes deposition of ice from a cloud at much higher temperatures than those required in the absence of smoke. The kinetics of deposition are less catastrophic in the presence of silver iodide, deposition occurring over an hour, which suggests that the larger particles act as nuclei for the growth of ice and that the time lag is associated with the polydisperse nature of the cloud of silver iodide; a large percentage of particles of the iodide were of diameter of order 30 Å, as determined by the electron microscope, in addition to many smaller particles and particles up to 1400 Å in diameter. Cwilong[21] has also found that silver iodide nuclei raise the ceiling temperature for ice formation, to $-2{\cdot}9° \pm 0{\cdot}1°$. Silver iodide could also be evaporated on to the polished surfaces of frost-point hygrometers and was most sensitive as a nucleator for ice deposition when in the form of an invisible film, deposition then occurring at $-2{\cdot}9° \pm 0{\cdot}05°$ in the form of ice at only a few points, with supercooled water between. At $-3{\cdot}1°$ deposition occurred as a mass of fine ice resembling emery. The silver iodide surface ages slowly and becomes less effective, and the coarse iodide gives a ceiling temperature for ice formation of $-5{\cdot}5°$.

Volcanic dusts, silicates, and clays have also been proved to act as nuclei for ice deposition. Solid carbon dioxide probably causes local cooling, resulting in ice precipitation, which will continue at the expense of supercooled water owing to the larger vapour pressure of the latter.

These phenomena are of importance in the study of meteorology, which is becoming an experimental science. As Dobson[22] has pointed out, there are few foreign nuclei present in air which can act as ice-forming nuclei above $-32°$, a larger number exist which can act in the range $-32°$ to $-41°$, and all particles of whatever kind can act below $-41°$, sodium chloride and metal dust, for example, being equally effective. Experiments suggest that the growth of ice is accompanied by the throwing off of small particles, probably ice crystallites, which can act as condensation nuclei. The problem of the formation of rain is related to these studies, since it is probable that all large rain drops, unlike drizzle, are formed from ice.

The Formation of Nuclei in Crystallisation from the Melt.—The pioneer work of Tammann[13] and his co-workers showed that the frequency of nucleation at first increases as a melt is cooled, passes through a maximum, and then decreases to zero. Nuclei formed under conditions of considerable supercooling grew too slowly to be observed but could be "developed" by warming to a higher temperature, at which the crystallisation velocity was finite but the tendency for spontaneous nucleation was small (compare the devitrification of glass). Some of Tammann's results are as follows: with betol (β-naphthyl salicylate) recrystallisation increased the number of

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[20] Vonnegut, *Chem. Reviews*, 1949, **44,** 277; *J. Appl. Physics*, 1947, **18,** 593; cf. also Reiss, *J. Chem. Physics*, 1950, **18,** 529; Bradley, *ibid.*, p. 1309.

[21] *Nature*, 1949, **163,** 727.

[22] *Proc. Physical Soc.*, 1950, *B*, **63,** 252; for a full summary of atmospheric precipitation, see Mason and Ludham, *Rep. Prog. Physics*, 1951, **14,** 147.

nuclei and so did the addition of anisic acid, whereas salicin depressed the number. Powdered emery, quartz, and fused feldspar increased nucleation, but glass and crystalline feldspar decreased it ; foreign particles also affected the crystal form appearing from the melt in the case of polymorphous materials. In general, the number of nuclei formed at one temperature was proportional to the time (but not with fatty acids and esters). Preheating greatly affects nucleation ; for instance, Othmer [23] found that with piperonal, m.p. 37°, the higher the temperature and longer the time of heating at 40—70° the smaller the number of nuclei on cooling, which Tammann interpreted in terms of " anisotropic molecules " existing after fusion but which are decomposed by heating.

Later workers have criticised both Tammann's technique and his interpretations, and have suggested that some of his experiments were vitiated by adventitious effects. If nucleation were an example of the application of probability laws, as Tammann believed, then the number of nuclei formed per second per cm.^{3} would be proportional to the time and independent of the volume, but this is not true.[24–27] Tammann's own result on the proportionality with time is considered by de Rooster to apply only to the region near the maximum. Many workers [26, 28, 29] have demonstrated the influence of preheating, and have given a more reasonable interpretation in terms of the effect of heat on inclusions, colloidal or otherwise, which could be coagulated, destroyed or dissolved on heating. Richards [30] believes that the inclusions form an adsorbed crystalline layer which persists after heating above the melting point (see below). More concordant results have been obtained after filtering the melt,[24, 31] for there is then a great decrease in nucleation frequency.

De Rooster [24] showed with salol that Tammann's technique did not give reproducible results, the nucleation numbers changing with the sample and decreasing on repetition of experiments. With α-bromopropionic acid it is possible to develop the nuclei at the same temperature as that of their formation, and again the nucleation numbers were not proportional to time. When the salol was filtered by a Jena filter with pores of 1 μ., the degree of supercooling possible without nucleation increased rapidly and salol could be kept indefinitely at room temperature in the liquid form ; a result not affected by recrystallisation, which disposes of the view that microcrystals persisted after melting the solid. Moreover, with filtered salol the degree of supercooling possible without the onset of crystallisation was not altered by heating for two hours at 100° ; nuclei began to form on cooling at — 65°.

Filtration provides a method for forming an " unstable " modification,

[23] *Z. anorg. Chem.*, 1915, **91,** 209.

[24] De Rooster, *Bull. Soc. chim. Belg.*, 1948, **57,** 187.

[25] Möller, *Physikal. Ber.*, 1925, **6,** 517.

[26] Hinshelwood and Hartley, *Phil. Mag.* 1922, **43,** 78.

[27] *Ann. Physik.*, 1938, **33,** 445.

[28] Marcelin, *Compt. rend.*, 1909, **148,** 631.

[29] Schaum, *Z. physikal. Chem.*, 1898, **25,** 722.

[30] *J. Amer. Chem. Soc.*, 1932, **54,** 479 ; Richards, Kirkpatrick, and Hutz, *ibid.*, 1936, **58,** 2243.

[31] Meyer and Pfaff, *Z. anorg. Chem.*, 1934, **217,** 257.

e.g., of salol or benzophenone, since the region of temperature which gives the " unstable " form is below its melting point, which is itself below the melting point of the " stable " form. Considerable supercooling is therefore necessary before the form unstable at higher temperatures can be crystallised, and filtration permits this, and increases the chances of obtaining the " unstable " form on cooling.

These studies emphasise the effect of inclusions, and are supported by the electrophoresis experiments of Hammer,[27] who found that after electrophoresis of the inclusions, nucleation in piperonal occurred round the cathode and not round the anode. Webster's experiments [32] on metals also support the emphasis on inclusions. Such experiments prompt the question whether any work done on liquid melts is free from vitiating effects, and make it difficult to find any relation between degree of supercooling and chemical composition. Fortunately, it is possible to remove the influence of these adventitious nucleation catalysts by breaking up the substance into micro-drops, whereupon the inclusions will be isolated and many drops will be free to give their spontaneous nucleation velocity. Vonnegut [33] followed the nucleation of drops of oxide-coated tin, 1—10 μ. in diameter, by volume changes, using " octoil " as a dilatometer fluid, and also studied water drops on a polystyrene film. Turnbull [34] used the dilatometer technique for mercury, gallium, lead, and bismuth, using protective films round the particles to prevent coalescence, and also studied a large number of supercooled pure metals on a microscope hot-stage, the particles of diameter 10—100 μ. (some 400 μ.) resting on freshly blown quartz or Pyrex glass, which by itself is unlikely to induce crystallisation. Vibrations were minimised, and an atmosphere of hydrogen, helium, or argon could be used, or the stage could be evacuated. Solidification could be followed by the appearance of a roughened surface, or for metals of high melting point by the " blick ", or sudden brightening on solidification. Whereas for bulk metals only a small supercooling has been observed, with the exception of iron and gallium, with isolated drops many drops showed large supercooling : *e.g.*, cobalt 330°, palladium 332°, aluminium 235°. The solidification region of temperature of the various drops of one batch ranged from the melting point to the maximum supercooling temperature, but the solidification temperature of one drop remained fixed for several, and usually all, cycles of successive heating and cooling ; the particles showing the maximum supercooling are alone of interest for simple theoretical studies, since the behaviour of the other particles was presumably due to inclusions.

The kinetic theory of nucleation may be applied to condensed phases if an allowance is made for the fact that atoms or molecules move relatively to their neighbours by jumps involving an activation energy E_D per molecule.

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[32] *Proc. Roy. Soc.*, 1933, *A*, **140,** 653.

[33] *J. Colloid Sci.*, 1948, **3,** 563.

[34] *J. Appl. Physics*, 1949, **20,** 817 ; 1950, **21,** 1022 ; *J. Chem. Physics*, 1950, **18,** 198, 768 ; *J. Metals*, 1950, **188,** 1144 ; " Thermodynamics in Physical Metallurgy ", Amer. Inst. Metals, 1950, Cleveland, Ohio, p. 282 ; Turnbull and Fisher, *J. Chem. Physics*, 1949, **17,** 71 ; Turnbull and Cech, *J. Appl. Physics*, 1950, **21,** 804 ; Fisher, Hollomon, and Turnbull, *ibid.*, 1948, **19,** 775 ; Hollomon, " Thermodynamics in Physical Metallurgy ", 1950, p. 161.

It would be expected that the nucleation rate in nuclei per cm.^{3} per second would be given by

$$I = k_0 \exp. - \left(\frac{E_D}{\boldsymbol{k}T}\right) \exp. - \left(\frac{\Delta G_{\text{max.}}}{\boldsymbol{k}T}\right) \quad . \quad . \quad (48)$$

where k_0 is a constant which may as an approximation be considered to be independent of temperature. For a cubic crystal of edge l

$$\boldsymbol{R}T \log \alpha = 4\sigma M/(\rho l), \quad \Delta G_{\text{max.}} = 2\sigma l^2 = 32\sigma^3 M^2/[\rho \boldsymbol{R}T \log \alpha]^2$$

i.e., equation (15) with $f = 6$, $\alpha = p/p_\infty$, where p is the vapour pressure of the melt and p_∞ that of the bulk solid. Moreover,

$$\log \alpha = \frac{\lambda_f}{\boldsymbol{R}}\left(\frac{1}{T} - \frac{1}{T_m}\right)$$

where λ_f is the molar heat of fusion, and T_m is the melting point. Hence

$$I = k_0 \exp. - \{32\sigma^3 M^2 T_m^2/[\boldsymbol{k}T\rho^2\lambda_f^2(T_m - T)^2]\} \exp.[- E_D/(\boldsymbol{k}T)] \quad . \quad (49)$$

$$= k_0 \exp. \{- A/[T(T_m - T)^2]\} \exp.(- B/T) \quad . \quad . \quad . \quad . \quad (50)$$

where $A = 32\sigma^3 M^2 T_m^2/(\boldsymbol{k}\rho^2\lambda_f^2)$ and $B = E_D/\boldsymbol{k}$.

Equation (50) gives a curve of the correct form, with a maximum given by

$$B/A = (3T - T_m)/(T_m - T)^3 \quad . \quad . \quad . \quad (51)$$

Gorsky,[35] using thin films on glass or mica, has found that equations (50) and (51) give a reasonable interpretation of experimental results on piperine (earlier data of Gorsky), the position of the maximum depending on the substrate ; agreement was also found with published data on sulphur and betol. For sulphur, Gorsky calculated an interfacial energy between the liquid and solid of 3·48 ergs cm.$^{-2}$. The term $e^{B/T}$ appears in the equation for viscosity as a function of temperature, in agreement with the view which has often been expressed that the increased viscosity resulting on lowering the temperature hinders the formation of nuclei ; however, a maximum in I will occur at $T = T_m/3$ even if $B = 0$.

Although such studies are of considerable interest, it is doubtful whether the phenomena observed do in fact refer to the spontaneous nucleation frequency. Moreover, the constant k_0 is left undefined. Turnbull [34] has applied transition-state theory to nucleation in condensed phases, in terms of the number of atoms or molecules of one phase in contact with the other across the nucleus boundary, a frequency factor $\boldsymbol{k}T/\boldsymbol{h}$ characteristic of transition-state theory, and an exponential term $\exp.[-\Delta G_{\text{max.}}/(\boldsymbol{k}T)]$. The treatment is similar to that of Becker and Döring [6] and gives the approximate result, in our terminology,

$$I = f n_c^{2/3}\left(\frac{f\gamma}{9\pi \boldsymbol{k}T}\right)^{1/2} n_1 \frac{\boldsymbol{k}T}{\boldsymbol{h}} \exp.[- (\Delta G_D + \Delta G_{\text{max.}})/(\boldsymbol{k}T)] \quad . \quad (52)$$

where ΔG_D is the free energy of activation for diffusion per molecule, n_1 is the number of atoms or molecules per c.c. in the mass of liquid, and the factor

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[35] *J. Exp. Theor. Physics, U.S.S.R.*, 1948, **18**, 45 (in Russian). The treatment is due to Frenkel but appears in an incorrect form in his book.[1]

$fn_c^{2/3}\left(\dfrac{f\gamma}{9\pi kT}\right)^{1/2}$ is approximately unity, giving as a further approximation

$$I = n_1\frac{kT}{h}\,\text{exp.}[-(\Delta G_D + \Delta G_{\text{max.}})/(kT)] \qquad . \qquad . \qquad (53)$$

Turnbull estimated that exp. $-[\Delta G_D/(kT)] = 10^{-2}$ approx., which gives $n_1(kT/h)\,\text{exp.}[-\Delta G_D/(kT)] \sim 10^{33\pm 1}$ sec.$^{-1}$ cm.$^{-3}$ as an approximately constant factor. Analysis of the thermal data for tin and mercury drops quoted above showed that log I was a linear function of $1/[T(T_m - T)^2]$, which follows theoretically by applying to equation (53) the same treatment as that which gave equation (50). From the linear plots,

$$n_1(kT/h)\,\text{exp.}[-\Delta G_D/(kT)]$$

was found to be $10^{30\cdot 9}$ for mercury and $10^{30\cdot 4}$ for tin, in sec.$^{-1}$ cm.$^{-3}$, in reasonable agreement with theoretical expectations ($10^{33\pm 1}$). The interfacial energies per cm.^{2} between solid and liquid for mercury and tin were calculated to be 24·0 and 54·5 ergs cm.$^{-2}$, respectively, spherical nuclei being assumed. Because of the high temperature-dependence of I, the onset of nucleation on cooling is sharp, corresponding to the observation that I is almost zero when $T_m - T < \delta$ but is very large for $T_m - T > \delta$, where δ is characteristic of the material; when, however, $T_m - T$ is sufficiently large, theory predicts that I will pass through a maximum and then decrease almost to zero. For most metals $(T_m - T)_{\text{max.}}$, *i.e.*, the maximum supercooling before the onset of crystallisation, is of the order $0{\cdot}18T_m$.

These results on micro-drops may be extrapolated to bulk material if the latter is free from inclusions. Mercury drops of diameter 4 μ. have a nucleation frequency for the whole drop (*i.e.*, $I \times$ volume of drop) of 10^{-5} sec.$^{-1}$ at $T_m - T = 60°$. Nuclei should form with the same frequency in drops of volume 1 cm.^{3} at $T_m - T = 49°$, if equation (53) applies. Experiment shows, however, that large masses of metal have rarely been supercooled to values of $T_m - T$ of this order (gallium and iron are rare examples), and this must be due to the presence of catalytic inclusions which prevent the achievement of large values of $T_m - T$. In agreement with this view, I for large masses of bismuth is dependent on the thermal history, but for small drops is independent.

Turnbull has also correlated the data on the drops of less fusible metals, with the results summarised in the following table, which applies to drops of 50 μ. diameter. The values of σ were calculated on the assumption of spherical solid nuclei. There is a rough constancy in the ratio $N_A\gamma/\lambda_f$, where N_A is Avogadro's number, which ratio ranges from 0·31 for antimony to 0·53 for mercury, with some indication that the elements fall into two groups, with ratios 0·33 and 0·5 approx. The value of σ for the interface solid–liquid water seems rather high in view of the similarity in structure between the two phases.

Data for supercooling of 50-μ. diameter drops (Turnbull [34])

Substance.	T_m, ° K.	$(T_m - T)_{\text{max.}}$	$(T_m - T)_{\text{max.}}/T_m$.	σ, ergs cm.$^{-2}$.	Ref.
Hg . . .	234·3	58	0·247	24·4	34
Ga . . .	303	76	0·250	55·9	,,
Sn . . .	505·7	105	0·208	54·5	33
Bi . . .	544	90	0·166	54·4	34
Pb . . .	600·7	80	0·133	33·1	,,
Sb . . .	903	135	0·150	101	,,
Al . . .	931·7	130	0·140	93	,,
Ge . . .	1231·7	227	0·184	181	,,
Ag . . .	1233·7	227	0·184	126	,,
Au . . .	1336	230	0·172	132	,,
Cu . . .	1356	236	0·174	177	,,
Mn . . .	1493	308	0·206	206	,,
Ni . . .	1725	319	0·185	255	,,
Co . . .	1763	330	0·187	234	,,
Fe . . .	1803	295	0·164	204	,,
Pd . . .	1828	332	0·182	209	,,
Pt . . .	2043	370	0·181	240	36
H_2O . . .	273·2	39	0·143	32·1	11

Turnbull has also made an interesting theoretical study of the effect of extraneous solids present, and considers that stable embryonic nuclei of the solid phase can be retained in the cavities of inclusions even above the melting point, *i.e.*, his theory resembles that of Richards [30] but is quantitative. The free energy of formation of a critical nucleus grown as a spherical cap, *i.e.*, a patch, on a plane surface may be shown to be f(θ) times the free energy of formation of a spherical nucleus, where θ is the contact angle and

$$\mathrm{f}(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2/4\ . \quad (54)\ \text{(cf. Volmer } ^1)$$

Turnbull writes for the nucleation frequency per sec. per cm.^{2} for catalysis due to such plane surfaces, applicable when all *cavity* embryos have been destroyed by heating above T_m,

$$I = n_s(\boldsymbol{k}T/\boldsymbol{h})\ \text{exp.}\{-\ k_1\sigma^3\mathrm{f}(\theta)/[(\Delta G_v)^2\boldsymbol{k}T]\}\ \text{exp.}(-\ \Delta G_D/\boldsymbol{k}T)\quad . \quad (55)$$

where n_s is the number of atoms of the melt per cm.^{2}, k_1 is a shape factor, ΔG_D is the free energy of activation per atom for diffusion across the liquid–solid interface, and ΔG_v is the free energy difference between the bulk phases, per unit volume of the solid ; $n_s\boldsymbol{k}T/\boldsymbol{h} \sim 10^{25\pm1}$ sec.$^{-1}$ cm.$^{-2}$, and hence the catalytic and non-catalytic reactions are distinguished by different temperature-" independent " factors. As inclusions are used up in the formation of nuclei, the nucleation rate at any one temperature may fall off with time, an effect observed with organic melts by Hammer [27] and discussed by Avrami.[37]

Inclusions with cavities can give rise to nucleation frequencies which have a thermal history, since crystal growth in the cavity may persist above T_m under conditions for which a nucleus on a plane surface would be unstable. The simplest shape of cavity is a cylinder, and for this form the free energy

[36] Mendenhall and Ingersoll, *Phil. Mag.*, 1908, **15**, 205.

[37] *J. Chem. Physics*, 1939, **7**, 1103.

of nucleus formation is given by

$$\Delta G = \pi r^2 h_1 \Delta G_v + 2\pi r\sigma[r(1 - \cos\theta)/\sin^2\theta - h_1 \cos\theta] \quad . \quad (56)$$

where r is the radius of the cylinder and h_1 its height. It may be shown that the nucleus is retained above T_m if $2\sigma \cos\theta/\Delta G_v > r$, *i.e.*, the solid phase will not be retained in the cavity of radius $> 2\sigma\cos\theta/\Delta G_v$ for any temperature above T_m. Once the nucleus has been removed by heating, it will have to reform in the cavity on cooling either at the bottom or on the sides, as a patch, and hence equation (55) will apply approximately. For gallium heated 5° above its melting point, embryonic nuclei are retained in cavities of diameter ≤ 140 Å (approx.) for $\theta = 60°$ (the contact angle between solid gallium and substrate) and these embryonic nuclei in cylinders are capable of growth at a supercooling of $\gtrsim 8{\cdot}5°$. It is to effects such as these that the curious phenomenon of " memory " must be ascribed, *viz.*, the retention of crystal orientation after repeated fusion and recrystallisation, presumably because of fixed cavities on the walls.

As a pendant to this section the curious phenomenon of " vapour snakes " may be mentioned. Phibbs and Schiff [38] found that if a glass ampoule of thoroughly degassed *cyclo*hexane was immersed in a mixture of solid carbon dioxide and acetone for a few seconds, the surface solidified to a crust, a thin glassy sheath of solid formed on the walls, and then a small vapour bubble formed below the crust. From this bubble of vapour a tubule of vapour grew into the liquid forming a " snake " 1 mm. in diameter, the tip travelling at 3 cm. per second until the whole of the liquid was filled. Crystallisation occurred round the wall of the " snake ". A very small quantity of air inhibited the effect. Frank [39] has suggested an explanation of this phenomenon.

The Formation of Nuclei in Supersaturated Solutions.—The formation of nuclei from solution is more complex than the process considered above since the following additional factors may play a part : diffusion, surface adsorption and double-layer formation, and desolvation of the solute on crystallisation. Controlled nucleation from solution is important in analytical procedures, which have been guided by the semi-empirical law of von Weimarn, according to which the concentration of nuclei is proportional to $(S - S_\infty)/S_\infty$, where S is the supersaturation and S_∞ the saturation concentration. In accordance with this law, large numbers of nuclei result from mixing concentrated solutions of, for example, manganese sulphate and barium thiocyanate, resulting in a gel.

The free energy of formation of a nucleus may be treated as before, with concentrations replacing vapour pressures, giving for the spherical nucleus

$$RT \log S/S_\infty = 2M\sigma/(\rho r_c) \quad . \quad . \quad (57)$$

In quantitative work activities must replace concentrations. Formulæ of this type have been verified by Hulett,[40] and by Dundon and Mack,[41] who found an increased solubility with decreasing particle size, and calculated

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[38] *J. Chem. Physics*, 1949, **17**, 843.

[39] *Ibid.*, 1950, **18**, 231.

[40] *Z. physikal. Chem.*, 1901, **39**, 385 ; 1904, **47**, 257.

[41] Dundon, *J. Amer. Chem. Soc.*, 1923, **45**, 2658 ; Dundon and Mack, *ibid.*, p. 2479.

interfacial tensions. Unfortunately, the more recent work of Cohen and Blenkingh [42] has shown that the solubility of barium sulphate is not influenced by particle size, and has revealed the necessity of very careful filtering of solutions containing particles before the concentration can be determined by electrical methods, since any particles coming through will vitiate the determination of concentration. This independence has been confirmed by Balarev,[43] and is probably due to unavoidable contamination; Balarev's views on crystal aggregates are, however, open to doubt (cf. Buckley [1]).

Supersaturation of soluble salts has usually been achieved by cooling a saturated solution. Jones and Partington [44] have studied theoretically the influence of temperature on the critical radius of a nucleus in equilibrium with a fixed concentration S at various temperatures. Their result may be deduced in a simple manner as follows: since

$$\log S/S_\infty = \frac{\lambda_s}{R}\left(\frac{1}{T} - \frac{1}{T_s}\right) . \quad . \quad . \quad (58)$$

where λ_s is the molar heat of solution for saturated solutions, assumed to be temperature independent, and S_∞ and S are the saturation concentrations at T and T_s, respectively, it follows from (57) that

$$T_s - T = 2M\sigma T_s/(\rho\lambda_s r_c) . \quad . \quad . \quad . \quad (59)$$

which is the desired relation (compare equation 16). Hence r_c decreases as the temperature falls, provided heat is absorbed on solution, and nucleation becomes more probable. The reverse will apply if heat is evolved on solution. Some evidence in support of equation (59) has been provided by Gopal,[45] who studied the degree of supercooling possible without crystallisation with various salts saturated at T_s and cooled to a temperature T at which crystallisation occurred. For some salts, *e.g.*, potassium nitrate and perchlorate, T remained constant after repeated heating and cooling, and there was a rough constancy in $\lambda_s(T_s - T)$ for different substances.

The work of Dehlinger and Wertz [46] on nucleation in solutions of alum showed that the time necessary for spontaneous crystallisation at 21° on cooling from 80° depended on the thermal history, the times being longer and better reproducible if the solutions were kept for longer times at 80°. This was not due to the formation of a colloid by hydrolysis, since the mixing of solutions heated for a long time at 80° and those heated for a short time gave a short time for nuclei to appear at 21°. The metastable region occurred at $< 3{\cdot}5$, $3{\cdot}8$, and $4{\cdot}0$ mole % at 0°, 21°, and 40°, respectively. Neumann and Miess [47] showed that these results could be interpreted in terms of an equation of the same form as equation (48), and deduced an interfacial energy, for an octahedral nucleus in a saturated solution, of 12·8 ergs cm.$^{-2}$. The work of Davies [48] on solutions of silver chloride also supports Ostwald's concept of a metastable region of concentration such

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[42] *Z. physikal. Chem.*, 1940, *A*, **186**, 257.

[43] *Kolloid Z.*, 1941, **96**, 19; 1942, **97**, 300.

[44] *Phil. Mag.*, 1915, **29**, 35.

[45] *J. Indian Chem. Soc.*, 1943, **20**, 183; 1944, **21**, 103.

[46] *Ann. Physik*, 1941, **39**, 226.

[47] *Ibid.*, 1942, **41**, 319.

[48] *Discuss. Faraday Soc.*, 1949, **5**, 103.

that for slightly greater concentrations precipitation is rapid, whereas for slightly less, the solutions, although supersaturated with $S/S_\infty \sim 1{\cdot}4$ at 25°, remain virtually stable for indefinite periods : the metastable limit of the solubility product was dependent on the initial ionic ratio $[Ag^+]/[Cl^-]$. Davies believes that growth may occur by particle coalescence.

Stauff [49] was able to count the actual nucleation rate with supersaturated potassium chlorate by means of a photocell technique. If we omit a term for edge energies, we obtain, by application of equation (48) to solutions,

$$\log I = X - Y/[T^3(\log S/S_\infty)^2] \quad . \quad . \quad . \quad (60)$$

where X and Y are constants. Results were in reasonable accord with this equation.

These studies suggest that the form of Becker and Döring's equation is correct when applied to solutions. The influence of surface charge differs from that in vapour systems, since colloidal particles in solution are likely to acquire a constant surface density of charge, independent of size and dependent on the concentrations of ions. As pointed out by Alexander and Johnson,[50] this implies that charge and surface tension act together. The effect of charge is, however, too small to account for the anomalous results for barium sulphate.[42]

The influence of foreign substances on nucleation is readily interpreted in terms of adsorption and alteration in the interfacial energy per cm.^{2}, although this is too facile an explanation to cover all phenomena. One of the most interesting addenda is " Calgon ", a polyphosphate, which if added in a few parts per million prevents the precipitation of calcium carbonate from solutions of the bicarbonate which have been boiled or made alkaline. The quantity of Calgon is too small for the effect to be due to complex formation.[51] Raistrick [52] believes the action of the Calgon to be due to the fact that the polyphosphate ions can fit on to a calcite lattice and hence prevent growth of an embryonic nucleus. In contrast to the long-chain polyphosphates, cyclic tri- and tetra-metaphosphate, with a rigid structure, do not prevent nucleation. Brooks, Clark, and Thurston [53] showed that when calcium chloride and sodium carbonate solutions are run into a crystalliser, with or without seed crystals of calcite, and with or without stirring, calcite, vaterite (μ-$CaCO_3$), or $CaCO_3,6H_2O$ may be formed depending on the concentration of Calgon, the temperature, and the degree of stirring ; under suitable conditions a new hydrate ($CaCO_3,H_2O$) may separate. These results show that metastable phases may appear as the result of an additive, Calgon, for example, preventing the crystallisation of calcite while nucleation and growth of $CaCO_3,6H_2O$ may proceed readily, another example of the limited applicability of the law of stages. Brooks, Clark, and Thurston consider that the influence of additives may be due not only to adsorption but also to absorption, the latter causing lattice distortion which may be revealed by X-rays. Lattice distortion can affect growth,

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[49] *Z. physikal. Chem.*, 1940, *A*, **187**, 107, 119.

[50] " Colloid Science ", O.U.P., 1949.

[51] Hatch and Rice, *Ind. Eng. Chem.*, 1939, **31**, 51.

[52] *Discuss. Faraday Soc.*, 1949, **5**, 234.

[53] *Phil. Trans.*, 1950, **243**, 145.

in which connection it should be remembered that the surface packing of a nucleus will differ from that of a bulk crystal even in the absence of additives, so that the simple kinetic-thermodynamic treatment of nucleation in solutions requires many refinements before it can deal adequately with the complex processes occurring with ions (cf. also Harbury [54]).

The Formation of Nuclei in Solids.—Much of the work on solid–solid transformations has been done on metal systems, and these will be briefly reviewed and will be followed by a section on solid reactions.

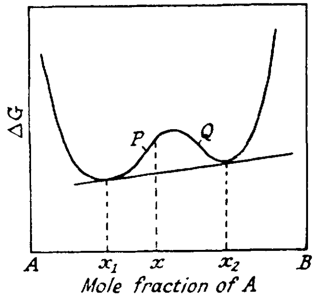

FIG. 5

Solid solutions of two metals may break up into two phases on cooling, *i.e.*, the free energy–composition curve assumes the form shown in Fig. 5. The appearance of the new phase can be followed by studying some physical property such as hardness or electrical resistance—for instance, the time for the electrical resistance to decrease to one-half of its initial value may be taken as a nucleation characteristic for the given temperature. The free energy of formation of a cubic nucleus of the new phase C (Fig. 5) formed by cooling a solid solution of composition x, say, may be written in the form

$$\Delta G = -\,n\Delta G_a + 6\gamma n^{2/3} + \phi n \qquad . \quad . \quad . \quad (61)$$

where $-\,\Delta G_a$ is the free energy change per atom involved in forming the new phase in bulk, and the last term allows for strain energy. Since the value of n for maximum ΔG is given by

$$n_c^{1/3} = 4\gamma/(\Delta G_a - \phi) \quad . \quad . \quad . \quad . \quad (62)$$

the inclusion of ϕ does not affect the form of the expression, and the factor ϕ will therefore be omitted.

Becker [55] has applied his nucleation theory to the behaviour of platinum–gold alloys, and writes for the rate of nucleation

$$I = k_0 \exp.\{-\,(E_D + \Delta G_{\text{max.}})/(kT)\} \qquad . \quad . \quad (63)$$

where E_D is an activation energy for diffusion, and k_0 is a constant (compare equations 48 and 53). The value of ΔG_a for any composition x may be calculated on a simple model involving only nearest-neighbour energy interactions and is given by

$$\Delta G_a(x) = Vzx(1 - x) + kT[x \log x + (1 - x) \log (1 - x)] \ . \quad (64)$$

where x is the mole-fraction of A, $V = V_{\text{AB}} - \frac{1}{2}(V_{\text{AA}} + V_{\text{BB}})$, where V_{AA} is the energy of the bond AA, etc., and where z is the co-ordination number. Similarly, the interfacial energy of the nucleus can be calculated in terms of V, giving (cf. Fig. 5 for the value of x_2)

$$\Delta G_{\text{max.}} = 2V(x - x_2)^2 n_c^{2/3} \qquad . \quad . \quad . \quad (65)$$

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[54] *J. Physical Chem.*, 1946, **50**, 190.

[55] *Ann. Physik*, 1938, **32**, 128 ; *Proc. Physical Soc.*, 1940, **52**, 71.

The value of V may be found from the temperature of critical mixing T_c, above which temperature a homogeneous phase alone is possible, since $kT_c = 0{\cdot}5zV$. For $x = 0{\cdot}15$, Becker has calculated the relative rates of nucleation below the temperature, 1211° K., at which separation of the new phase first begins, taking $E_D = 39{,}000$ cals. per mole, and finds that I passes through a maximum 300° below the equilibrium temperature, in reasonable agreement with the experiments of Johansson and Hagsten,[56] who found from the electrical resistance a maximum at $\Delta T = 350°$ C. Hardy [57] has shown that the resistance of lead–tin alloys changes with time in a manner explicable on Becker's theory, except over the region for which the plot of log (time of half change of resistance) against $1/T$ is linear. An alternative hypothesis due to Borelius [58] applies in this region ; between the points of inflexion P, Q of Fig. 5, $\mathrm{d}^2G/\mathrm{d}x^2$ is negative, and this implies that negative or " uphill " diffusion may occur in this region, if the driving force for diffusion is considered to arise from a gradient of activity rather than one of concentration. Any concentration differences arising from fluctuations are then accelerated, giving a new phase which may be termed a segregate, formed by a change of composition in the parent lattice but without a change of structure, in contrast to a precipitate proper. No activation energy is needed for this process other than that required for diffusion, and hence the time of half-change of resistance is a linear function of inverse temperature.

Turnbull and his co-workers [34] have emphasised that transient nucleation phenomena are possible in which the steady state has not been reached, *i.e.*, a nucleation incubation period may be observed. Such transient phenomena are likely to appear on quenching solid solutions. These authors distinguish " thermal nuclei " which grow at constant temperatures and " athermal nuclei " which appear only when the temperature is changing, and arise, for example, from the fact that some of the nuclei present as a fluctuation phenomenon above the transformation temperature (*e.g.*, T_m for liquid–solid transitions) may, if the specimen is sufficiently quenched, act as growth nuclei although the natural rate of thermal nucleation at such a low temperature may be effectively zero. Similarly, a reaction may proceed by thermal nucleation at one temperature, and, on quenching, by athermal nucleation at another. Such changes may occur in the transformations austenite → martensite, body-centred cubic → face-centred cubic lithium.

Some work has been reported by Lotmar [59] on the growth of crystals of antimony from " amorphous " antimony vacuum-sublimed on glass [cf. Fig. 6 (*a*)]. There is also an extensive literature on the recrystallisation of cold-worked metal on annealing, and on the nucleation of magnetic domains in a crystal, which because of their special character will not be considered here.

Nucleation occurs in solid reactions of the type solid → solid + gas by the start of the reaction at a point on the crystal surface, and from this point an interface spreads out. When the nuclei have grown to a size visible under the microscope they are found to have characteristic shapes ;

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[56] *Ann. Physik*, 1937, **28**, 520.

[57] *J. Inst. Metals*, 1950, **77**, 417.

[58] *Ann. Physik*, 1938, **33**, 517.

[59] *Helv. Physica Acta*, 1945, **18**, 369.

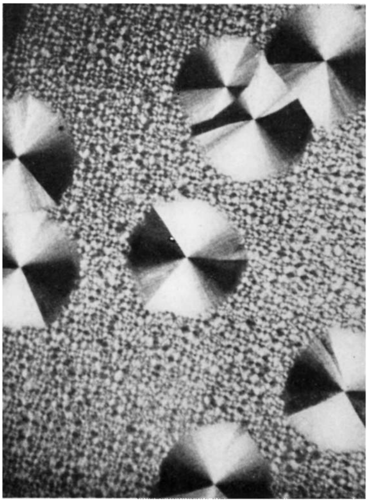

FIG. 6 (*a*)

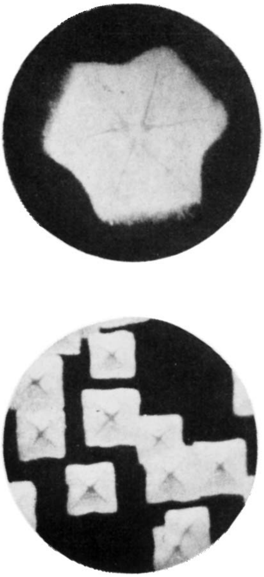

FIG. 6 (*b*)

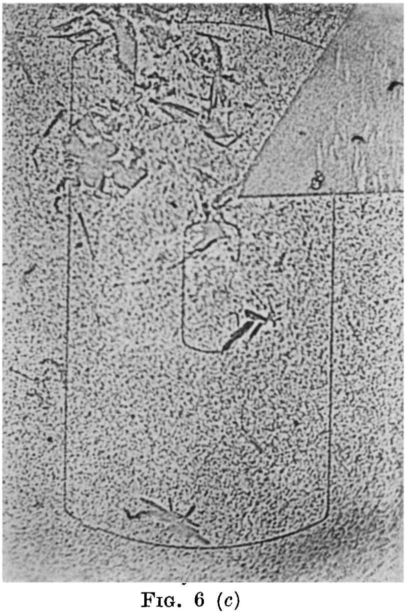

FIG. 6 (*c*)

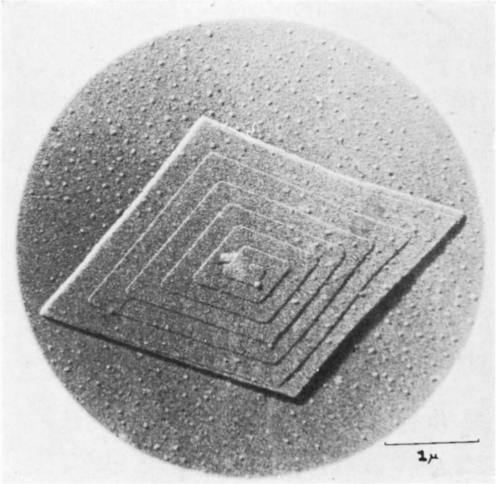

FIG. 6 (*d*)

dehydration of the alums gives square nuclei on the 100, rhombic on the 011, and hexagonal on the 111 faces [cf. Fig. 6 (*b*), due to Garner and his co-workers,[60] which shows hexagonal and square nuclei on potassium alum]. It appears from the work of Garner and Cooper [61] that nuclei may grow abnormally slowly at first, which these authors suggested might be due to the influence of interfacial tension on reaction velocity. An alternative suggestion has been made by the Reviewer [19] in terms of the effect of curvature on activation energy, and more recent work [60] has shown that the phenomena are more complex than was at first considered.

Nucleation is a possible explanation of false equilibria, as was suggested by Zawidski and Breitsnajder,[62] who showed that, in the formation of calcium carbonate from lime and carbon dioxide, pressures greater than equilibrium may be observed, due to a number of small nuclei of calcium carbonate.

In exothermic reactions there are often no observable signs of nucleation ; *e.g.*, mercury fulminate on decomposition becomes yellow throughout the crystal,[63] and potassium azide becomes blue ; α-lead azide, however, forms nuclei of lead on the surface, in contrast the β-form for which the nuclei are more diffuse.

Although in solid reactions the nucleation rate is often constant, suggesting an explanation in terms of chance accumulations of energy, occasionally, *e.g.*, with $NiSO_4,7H_2O$, the number of nuclei is proportional to the square of the time, and recent work [60] has shown that nucleation may cease after a time, suggesting that the nuclei are pre-formed on some type of strain point or impurity centre.

Section II. Two-dimensional nucleation

The Classical Theory of Nucleation.—The theory of two-dimensional nucleation is concerned with growth on crystal faces which have already been formed. We should expect by analogy with the phenomena in three dimensions that a small group of atoms on a perfect crystal face will evaporate unless a sufficient degree of supersaturation is reached. At low degrees of supersaturation the critical two-dimensional nucleus would be relatively large and the improbability of its formation would be reflected in very slow or unobservable growth.[64] The theory for perfect crystals has been developed by Volmer, and by Stranski and Kaischew [65] and Becker and Döring,[6] but it must be emphasised that direct comparison with experiment is not possible since no nuclei on a growing crystal have been counted, and we have to compare the observed and theoretical rate of growth. The *theory* is confined to growth from the vapour.

The free energy of formation of a two-dimensional nucleus containing n molecules is given by

$$\Delta G(n) = -nkT \log \alpha + \eta g n^{1/2} \quad . \quad . \quad . \quad (66)$$

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[60] Acock, Garner, Milsted, and Willavoys, *Proc. Roy. Soc.*, 1947, *A*, **189**, 508.

[61] *Trans. Faraday Soc.*, 1936, **32**, 1739 ; Bradley, ref. (19).

[62] *Z. physikal. Chem.*, 1933, *B*, **22**, 60.

[63] Garner, *Science Progress*, 1938, **33**, 209.

[64] Mott, *Nature*, 1950, **165**, 295.

[65] Volmer, *Physikal. Z.*, 1921, **22**, 646 ; Stranski and Kaischew, *ibid.*, 1935, **36**, 393.

where η is the edge energy *per molecule* and g is a packing factor such that the number of molecules in the edge of a nucleus containing n molecules is $gn^{1/2}$. It follows that the critical number of molecules is given by

$$n_c^{1/2} = \eta g/(2\boldsymbol{k}T \log \alpha) \quad . \quad . \quad . \quad . \quad (67)$$

and

$$\Delta G_{\text{max.}} = \tfrac{1}{2}\eta g n_c^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (68)$$

For a circular nucleus this corresponds to a critical radius ρ_c' given by

$$\rho_c' = a\eta/(\boldsymbol{k}T \log \alpha) \quad . \quad . \quad . \quad . \quad (69)$$

and for a square nucleus of edge L_c this is given by

$$L_c = 2a\eta/(\boldsymbol{k}T \log \alpha) \quad . \quad . \quad . \quad . \quad (70)$$

where a is the lattice spacing.

We may suppose that the nuclei can be built up directly by collision from the vapour, or we can adopt the more likely hypothesis (cf. Volmer [1]; G. P. Thomson [66]) that molecules can move by activated diffusion over the whole surface, which is therefore available for the growth of nuclei. Nuclei grow by accretion of molecules by collisions in the surface. If A_1 is the adsorption energy of such mobile molecules, the surface concentration in equilibrium with a bulk pressure p_∞ is given by

$$c_1 = a^{-2} \exp.(-W + A_1)/(\boldsymbol{k}T) \quad . \quad . \quad . \quad (71)$$

since $1/a^2$ is the surface concentration of molecules *in* the plane face and W is the heat of vaporisation per molecule. When the vapour pressure is p the surface concentration is $c_\alpha = \alpha c_1$, if the surface concentration is assumed proportional to bulk pressure (otherwise Langmuir's adsorption isotherm may be assumed). Since an adsorbed molecule moves a distance $\nu a \exp.[-U_D/(\boldsymbol{k}T)]$ cm. per second, where U_D is the activation energy for diffusion, and since $2a$ is the " collision length ", the number of collisions per second per cm.^{2} in the surface is

$$C = \tfrac{1}{2}c_\alpha^2 . 2a . \nu a \exp.[-U_D/(\boldsymbol{k}T)] \quad . \quad . \quad . \quad (72)$$

If we apply the three-dimensional treatment to the surface, the steady nuclear current in nuclei per cm.^{2} per second is given by

$$I = C[\eta g/(8\pi \boldsymbol{k}T n_c^{3/2})]^{1/2} \exp.[-\Delta G_{\text{max.}}/(\boldsymbol{k}T)] \quad . \quad . \quad (73)$$

This theoretical prediction may be compared with Volmer and Schultze's experimental results [67] on iodine, naphthalene, and phosphorus. Using as a source of vapour the solid at a slightly higher temperature than that of the growing crystal, these authors found that crystal growth continued on iodine at $\alpha >$ app. 1·01, and for naphthalene and phosphorus there appeared no nucleation necessary down to $\alpha \sim 1{\cdot}001$. In contrast, equations of the type (73) predict that crystal growth on a perfect surface will not continue unless $\log_e \alpha$ is of the order unity. The various treatments given by different authors all contain the term $\exp.[-\Delta G_{\text{max.}}/(\boldsymbol{k}T)]$, which is the controlling one, and variations in the pre-exponential factor have little effect on the value of I in comparison. Although at first sight predicted and experimental

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[66] *Proc. Physical Soc.*, 1948, **61**, 403.

[67] *Z. physikal. Chem.*, 1931, *A*, **156**, 1.

values of α seem of the same order, yet the values of $\log \alpha$ are very different and there is a very large discrepancy between theory and experiment, as first pointed out by Frank.[68] Refinements of the theory which allow for curvature of the crystal nucleus, and a more refined treatment of diffusion do not affect the issue,[69] and it appears that crystals will grow at low supersaturations although they are formed as three-dimensional nuclei at comparatively high supersaturations. Further experimental work on growth of crystals from the vapour is, however, desirable ; *e.g.*, for iodine there are only a few points on the graph [67] of growth rate versus supersaturation.

It may be noted that Becker and Döring considered also the necessity for linear nucleation, *i.e.*, the edge of a nucleus could not advance unless a group of molecules formed on the edge. This is unnecessary, since it is readily shown that there will be sufficient " Frenkel kinks " in the edge to act as growth points.

Frank's Theory of Surface Nucleation.—Frank supposes that crystal growth does not require the type of nucleation demanded by Becker and Döring's theory, since crystal imperfections are always present and can induce growth at values of near to unity. Burgers's screw dislocation [70] gives a self-perpetuating edge, in contrast to a step on a perfect crystal face which would grow out and disappear. The effect of a screw dislocation on a crystal may be visualised by cutting a block of rubber in the plane *ABCD* (Fig. 7), and the portion *ABCDEFGH* is then pushed upwards relatively to the rest of the cube ; the top surface then becomes distorted and shows an edge along *AB*. This edge would persist however many molecular layers are deposited on the face.

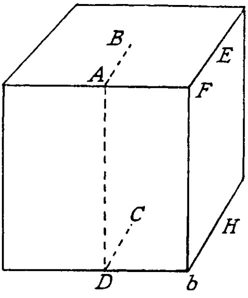

FIG. 7

The line *BC* is the axis of the screw dislocation, since displacements of the molecules along this line repeat after a rotation of 2π about the axis. The successive layers form a helix which may be right- or left-handed. Such dislocations, or displacements compounded of the " edge " and " screw " type, may be formed owing to inclusions or between mosaic blocks.

According to Frank, the " winding up " process of crystal growth is not simply the rotation of the step, but the formation of curved edges to the step. The result is a spiral form. The curvature arises from the rounding of the corner in the centre, and growth in this region is delayed until the radius of curvature equals ρ_c' : the rest of the step has moved on and hence a curved step results. A simple explanation of the effect of curvature on growth is that a convex-curved step of radius ρ' has a greater

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[68] *Discuss. Faraday Soc.*, 1949, **5**, 48. Cf. also Burton, Carbrera, and Frank, *Phil. Trans.*, 1951, *A*, **243**, 299.

[69] Burton and Carbrera, *Discuss. Faraday Soc.*, 1949, **5**, 33, 40.

[70] *Proc. K. Akad. Wetensch. Amsterdam*, 1939, **42**, 293 ; Frank, *Phil. Mag.* 1951, **42**, 809.

two-dimensional vapour than a straight step, and is in equilibrium with a surface concentration greater than c_1, say c_1', where

$$\boldsymbol{k}T \log (c_1'/c_1) = a\eta/\rho' = \boldsymbol{k}T(c_1' - c_1)/c_1 \text{ for small values of } (c_1' - c_1)/c_1 \quad (74)$$

It follows that the linear rate of growth $v(\rho')$ will be proportional to $(c_\alpha - c_1')$ and not to $c_\alpha - c_1$ (which would apply for a straight step) and hence

$$v(\rho') = v(\infty)(c_\alpha - c_1')/(c_\alpha - c_1) \quad . \quad . \quad . \quad . \quad (75)$$

$$= v(\infty)\{1 - a\eta/[\rho'\boldsymbol{k}T(\alpha - 1)]\} \quad . \quad . \quad . \quad (76)$$

by using (74) and putting $c_\alpha = c_{1\alpha}$.

But $\rho_c' = a\eta/(\boldsymbol{k}T \log \alpha) = a\eta/[\boldsymbol{k}T(\alpha - 1)]$ if $(\alpha - 1)$ is small. Hence

$$v(\rho') = v(\infty)(1 - \rho'/\rho_c') \quad . \quad . \quad . \quad . \quad (77)$$

Hence $v(\rho')$ rises from zero to $v(\infty)$ as ρ' rises from ρ_c' to infinity. The concept of the critical radius is thus retained but plays a special part in Frank's theory.

Dislocation edges may run either from the point of emergence of the axis to the edge of the crystal, or between two dislocation axes of dislocations of opposite orientation. If the distance from the crystal edge to the point of emergence of the dislocation screw axis, or the distance between two points of emergence, is too small for a given supersaturation, continuous growth will not occur, sence the step will assume the shape of a portion of the critical nucleus, and will then stop growing. A useful rule is that the critical nucleus must be capable of being slipped between the point of emergence of the axis and edge or between the two points of emergence of the axes. A curious paradox results, since dislocations are necessary for growth at low supersaturations, but too high a surface concentration of dislocations is unfavourable to growth.

Griffin [71] has obtained remarkable experimental confirmation of Frank's theory by photographing patterns similar to those postulated by Frank. Growth forms are visible as diffraction edges on beryl (cf. Fig. 6 (*c*), due to Griffin) when an ordinary metallurgical microscope is used slightly out of focus and with a magnification of 500—1050. They are of the same shape but of different visibility when viewed untouched or when silver is deposited on them *in vacuo* according to Tolansky's technique,[72] although the silver layer is 250—500 Å thick and the steps are only 7·9 Å. Interferometric studies show that the steps are less than 34 Å high, and from the fact that no visible kink appears when an interference fringe crosses a step, it follows that the steps are less than 20 Å high. Steps are split by inclusions and recombine on the other side, the same number of steps occurring on each side of the inclusion, so that the steps are probably unimolecular, *i.e.*, 7·9 Å high. Crystals from the Urals and California show the same type of result. The density of screw dislocations varies considerably on different areas of the same face and on equivalent faces of the same crystal, *e.g.*, there are 100 screw dislocations per $7{\cdot}6 \times 10^{-3}$ mm.^{2} on one face, and on other parts several sq. mm. with no dislocations.

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[71] *Phil. Mag.*, 1950, **41,** 196; 1951, **42,** 775.

[72] " Multiple Beam Interferometry of Surfaces and Films ", O.U.P., 1948.

The safety-razor-like shapes revealed by Griffin may be explained in terms of a variation in growth rate as a function of orientation. Frank[73] deduces from the spacing between the forms that a supersaturation of about 1% caused the growth on beryl, whereas growth forms on synthetic emerald grown hydrothermally by Nacken (cf. van Praagh[74]) show that the natural crystal probably grew at about two-thirds of the absolute temperature of the artificial crystals. Presumably it will be possible in future work to deduce edge energies from the study of crystals grown from solutions of known supersaturations.

Dawson and Vand[75] have published a photomicrograph [cf. Fig. 6 (*d*)] of a spiral growth form on small crystals of *n*-hexatriacontane, $C_{36}H_{74}$, grown from a solution in light petroleum, and examined in a Philips electron microscope (shadow cast with palladium). Verma[76] and (independently) Amelinckx[77] have photographed spiral growth forms on carborundum crystals.

It will have been observed that Frank's theory, which properly applies only to growth from the vapour, has been used to explain results on growth from solution. The complexity of the latter process can be seen from the fact that it is possible to have one face stationary while the others are growing, but such effects are outside nucleation theory and will not be considered here.

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[73] *Phil. Mag.*, 1950, **41**, 200.

[74] *Research*, 1948, **1**, 458.

[75] *Nature*, 1951, **167**, 476 ; *Proc. Roy. Soc.*, 1951, *A*, **206**, 555.

[76] *Nature*, 1951, **167**, 939 ; **168**, 430 ; *Phil. Mag.*, 1951, **42**, 1005 ; Frank, *ibid.*, p. 1014.

[77] *Ibid.*, **167**, 939 ; **168**, 431.