

## The Mechanism of Ice Crystal Growth and Habit Formation

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### ABSTRACT

The formation of multiple layers of adsorbed water molecules on the basal and prism faces of ice may be responsible for the remarkable temperature dependence of all growth variables (linear growth rate, step velocity, and mean migration distance). This effect results from an increased residence time of molecules in the adsorbed state as the melting point is approached. A quantitative treatment based on the Brunauer, Emmett and Teller model of multi-layer adsorption exemplifies these concepts and appears to explain the measured trends with temperature. When the theoretical treatment is used in conjunction with a growth model based on the propagation of spiral steps, reasonable values for the condensation coefficient emerge. The alternation of the primary habit of ice crystals with temperature is explained when the theoretical treatment is applied to the basal and prism faces, respectively.

### 1. Introduction

Understanding the mechanism by which individual molecules ultimately become members of a crystal lattice is a basic goal of all crystal growth studies. The growth mechanism is the total picture of the growth process which gives physical meaning to growth data. When correct, it enables us to extrapolate the available data to other, more general sets of conditions and thereby to serve as a prediction tool. In addition to providing a detailed description of events on a particular crystal face, the molecular mechanism of growth is also the basis for the formation of the macroscopic crystal habits, since the habit is nothing but an integration of the relative growth rates of the individual faces. In building up the macroscopic crystal, interactions arise between the microscopic surface processes and the macroscopic geometry of the crystal due to the limited rates of mass and heat transfer through the environment. These interactions produce a wide variety of intricate crystal forms, characteristic of ice crystals grown naturally.

The mechanism by which water vapor molecules become incorporated into ice crystals is important in atmospheric precipitation processes and has been investigated by many from several points of view. Individual ice crystals have been grown artificially in the laboratory and collected in the real atmosphere; their habits and rates of growth have been measured as

functions of the growth temperature with the intention of formulating some generalities regarding the growth process. In light of recent measurements of the linear growth rates of individual basal and prism faces (Lamb and Hobbs, 1971; Lamb and Scott, 1972), it is possible to develop a coherent picture of ice crystal growth which satisfies much of the presently available data on the growth of ice from the vapor phase and which is, moreover, consistent with our general concepts of surface structure and the growth of other substances.

The general features of previous investigations may be broken down into studies of habit, studies of growth rates, and studies of step parameters. Nakaya (1954) showed that the habits of ice grown in air are a complicated function of supersaturation and temperature. However, Kobayashi (1961) found that these variations in shape may be subdivided into two broad classifications: primary habits, which depend mainly on temperature; and secondary features, which are strongly dependent on supersaturation. The secondary features appear superimposed upon the basic primary habit in the presence of external diffusion fields containing strong gradients of moisture or temperature. A peculiar characteristic of ice is the tendency for the primary habit to alternate between plates and columns as the temperature is lowered from the melting point; the transition temperatures are roughly  $-4$ ,  $-9$  and  $-20^{\circ}\text{C}$ . This alternation of the primary habit is a manifestation of the strange dependence on temperature of the linear growth rates of the individual faces. Indeed, the works of Lamb and Hobbs and of Lamb

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and Scott present measured values of the linear growth rates which show these alternations in terms of maxima and minima in the growth curves.

It should be realized, however, that it is only the relative growth rates which are of concern in understanding the origins of the primary habits. A convenient measure for the relative rates is the condensation coefficient  $\alpha$  defined by

$$G = \alpha G_{\max}, \tag{1}$$

where

$$G_{\max} = \Omega \delta F \tag{2}$$

is the maximum growth rate possible at the net impingement flux  $\delta F$ , and  $\Omega$  is the volume of a water molecule in the lattice. The net impingement flux is related to the local supersaturation  $s$  by

$$s = \frac{\delta F}{F_s(T)}, \tag{3}$$

where  $F_s(T)$  is the molecular flux hitting the surface at equilibrium. If  $\delta P$  is the corresponding excess vapor pressure, then from the kinetic theory of gases

$$\delta F = \frac{\delta P}{(2\pi mkT)^{\frac{1}{2}}} \equiv k_T \delta P, \tag{4}$$

in which  $k$  is Boltzmann's constant,  $k_T$  is defined as the kinetic theory factor,  $m$  is the mass of a water molecule, and  $T$  the temperature. From these equations the condensation coefficient can be calculated from linear growth rate data at known values of temperature and excess pressure (supersaturation). The trends with temperature so obtained from the data of Lamb and Scott are shown in Fig. 1. The overall trends to these curves are, of course, similar to those of the linear growth rates and cross at the temperatures ( $-5.3$  and  $-9.5^\circ\text{C}$ ) which define the transitions between the primary habit regimes of plates and columns within the data range (Lamb and Hobbs, 1971).

The condensation coefficient may be interpreted as the fraction of impinging vapor molecules which are successful at actually being incorporated into the ice lattice. The trends of Fig. 1 thus show how strongly the probability of incorporation varies with temperature on the basal and prism faces of ice. As indicated by Lamb and Hobbs, it may be just these strong variations in the crystallographic growth parameter  $\alpha$  which give rise to the peaks in the rate at which an ice crystal accumulates mass (Hallett, 1965; Fukuta, 1969). Of particular interest, too, is the tendency for the condensation coefficient of both faces to approach unity as the temperature approaches  $0^\circ\text{C}$ , the melting point of ice.

The condensation coefficients for the two main low-index faces of ice (prism and basal) do "explain" many aspects of the observed crystal habits and mass growth rates, but, even so, the physical basis behind the peculiar trends in the condensation coefficients them-

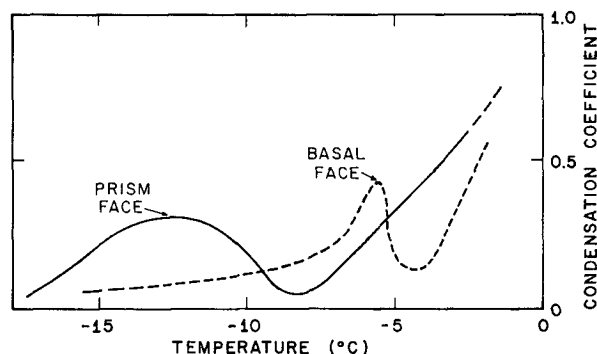


FIG. 1. The condensation coefficient of ice calculated from the linear growth rate data of Lamb and Scott (1972).

selves remains to be uncovered. As pointed out by Lamb and Hobbs and discussed in detail by Lamb and Scott, there exists a basic similarity in the shape of the trend to the linear rates (or condensation coefficients) and the measured velocities of step propagation across the basal face (Hallett, 1961; Kobayashi, 1967). This, it was suggested, implies an indirect correlation between the step velocity  $v$  and the frequency  $f$  at which steps are generated on the face since the step velocity  $v$  itself is not directly coupled with the rate  $G$  at which the face advances parallel to itself. The spiral step mechanism of Frank (1949) was invoked as being the simplest mechanism which allows a natural physical relation between  $G$ ,  $f$  and  $v$ . Then, if the steps gather adsorbed molecules from within a limited distance from the step, all of the growth parameters may be qualitatively explained. This catchment distance is usually taken to be the mean migration distance on the surface,  $x_s$  (Mason *et al.*, 1963). It is the purpose of this paper to reconsider this basic parameter and at the same time develop a total picture of the growth process, both qualitatively and quantitatively.

## 2. Previous attempts to understand $x_s$ .

Previous attempts to explain the measured temperature dependence of the step velocity  $v$  and the mean migration distance  $x_s$  have not been wholly successful. The crucial parameter  $x_s$  is a function of the mean time  $\tau$  that a typical molecule resides in the adsorbed state:

$$x_s^2 = D_s \tau, \tag{5}$$

where

$$D_s = D_0 \exp(-U/kT) \tag{6}$$

is the surface diffusion coefficient and  $U$  the activation energy. The residence time

$$\tau = \tau_0 \exp(W/kT) \tag{7}$$

is the inverse of the desorption constant used by Hobbs and Scott (1965), where  $W$  is the energy of attachment to the surface. However,  $W$  is expected to be greater

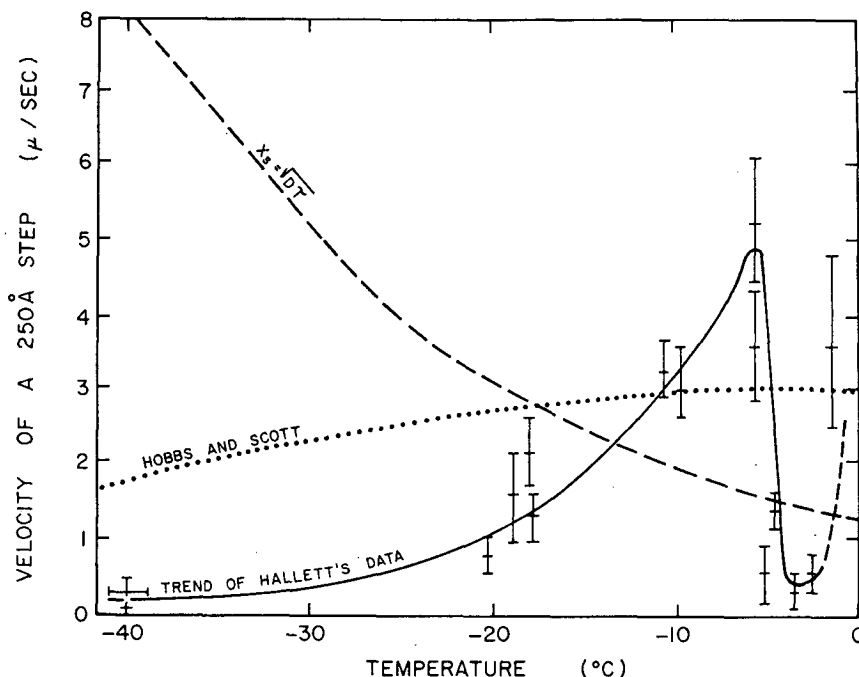


FIG. 2. Comparison of different theoretical growth parameters with the experimental data of Hallett (1961).

than  $U$  so that the calculated values of  $x_s$  decrease with increasing temperature, with the trend shown by the dashed line in Fig. 2. If step velocity  $v$  is proportional to  $x_s$ , such a trend clearly contradicts the experimental results of Hallett, shown as the solid curve. To counter this tendency and force  $x_s$  to have the more desirable upward trend with temperature, Mason *et al.*, suggested that the values of  $U$  and  $W$  in Eqs. (6) and (7) are each strong functions of temperature and, moreover, contain a discontinuity at the appropriate temperature which generates the maximum and minimum.

To provide a more plausible explanation, Hobbs and Scott considered the possibility that molecules already on the surface hinder the subsequent adsorption of other molecules, giving rise to a so-called "blanketing" effect. This had the effect of defining a new step collection distance with a slightly improved temperature dependence (note the trend in the dotted velocity curve in Fig. 2). However, at the low supersaturations usually used it can be shown that the "blanketing" effect is insignificant. Thus, this approach, too, is unable to explain the strange temperature trends to  $x_s$  or  $v$  in a satisfactory manner.

In a simplified way, the trends with temperature of all of the growth variables (linear growth rates, step velocity, and migration distance) may be thought of as a superposition of a strong average trend upward with increasing temperature together with a nearly discontinuous change between each maximum and associated minimum. As suggested by several authors (Mason

*et al.*, 1963; Ryan and Macklin, 1969) it is very likely that two independent phenomena are responsible for the net effect. The discontinuity, the origin of the maximum and minimum, is often considered to be an effect of a surface reorientation or Faraday's so-called "quasi-liquid" layer (Weyl, 1951; Fletcher, 1962, 1968). Most studies of the behavior of steps on ice, however, have been concerned with the average upward trend and this is also a prime purpose of the present work.

### 3. The effects of multi-layer adsorption

#### a. The adsorption model

Previous treatments of the adsorption of molecules onto the surface of ice have considered only monolayer or Langmuir adsorption, with a single adsorbate-solid interaction (Hobbs and Scott, 1965). It is this simple adsorbate-solid interaction, via Eq. (7), which most likely results in an unacceptable trend in  $\tau$  and in  $x_s$  with temperature. It is, however, readily accepted that in many adsorption systems the interactions between the adsorbed molecules themselves can virtually dominate the interactions with the underlying solid and lead to very large effective residence times. This occurs in multi-layer adsorption especially at pressures approaching the liquid condensation pressure. Of course, when liquid begins to form on the surface the number of adsorbed molecules and the residence time increase virtually without bound. Since water vapor adsorbs in multi-layers in some systems (Gregg, 1942), it seems

reasonable to expect such adsorption on its own solid, ice. In addition, it is very interesting that as the temperature of a crystal approaches its melting point, the pressure of vapor in equilibrium with the solid steadily and naturally approaches that in equilibrium with the supercooled liquid. This means that, if multi-layer adsorption of water vapor can occur on ice at all, new possibilities arise for helping us understand the growth characteristics of ice crystals.

In order to develop this picture more quantitatively, consider the model of multi-layer adsorption developed by Brunauer, Emmett and Teller (1938). In utilizing this BET theory we realize that it has many failings but, nonetheless, it does describe a number of adsorption systems quite well. In any case, the intent of the following treatment is to present a quantitative *example* of multi-layer adsorption which fits our physical picture. The effects we are trying to illustrate would arise from any model in which the concentration  $n$  [cm<sup>-2</sup>] of adsorbed molecules increases with increasing pressure sufficiently strongly near the liquid condensation pressure. The approach to the liquid condensation pressure is usually specified by the relative pressure,

$$X \equiv \frac{P}{P_L(T)}, \tag{8}$$

where  $P$  is the vapor pressure in dynamic equilibrium

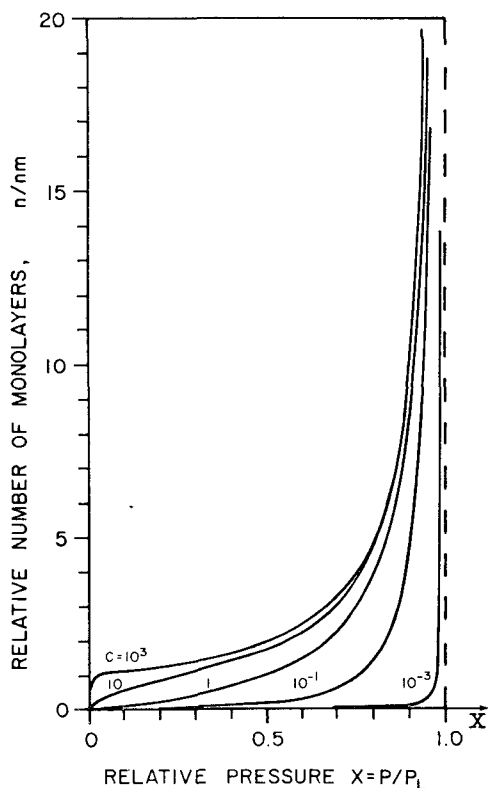


FIG. 3. Adsorption isotherms for various values of the adsorption parameter  $C$ , according to the model of Brunauer *et al.* (1938).

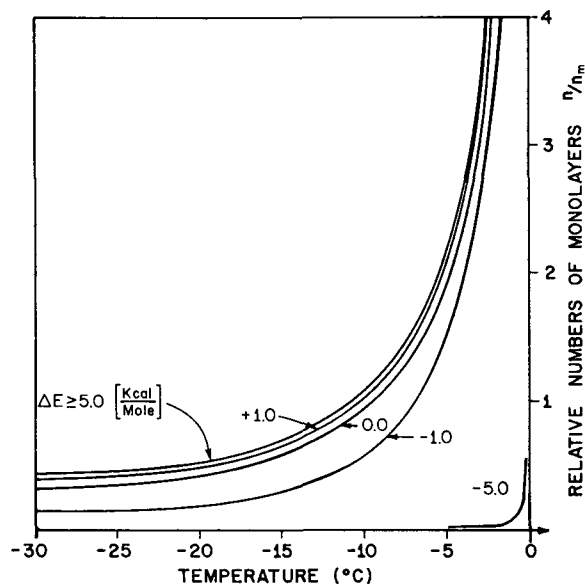


FIG. 4. The composite dependence of surface coverage  $n/n_m$  on temperature for different values of  $\Delta E = E_1 - E_L$ .

with the adsorbed layer and  $P_L(T)$  a reference pressure which is usually considered to be in equilibrium with the supercooled liquid state. Generally, when the solid is growing,

$$P = P_s(T) + \delta P, \tag{9}$$

where  $P_s(T)$  is the equilibrium vapor pressure of the solid and  $\delta P$  the experimentally determined excess pressure. The relative pressure  $X$  is thus a well-defined, monotonic function of temperature and, for small supersaturations, approaches unity as the melting point of the solid is approached.

In the BET model the total surface concentration of adsorbed molecules is given by

$$n = \frac{n_m C X}{(1-X)[1+(C-1)X]}, \tag{10}$$

where  $n_m$  is the number of adsorption sites on the solid [cm<sup>-2</sup>], and

$$C = C(T) = C_0 \exp[(E_1 - E_L)/kT] \equiv C_0 \exp(\Delta E/kT) \tag{11}$$

is an adsorption parameter which characterizes the system. In (11)  $E_1$  is the energy binding the first adlayer<sup>2</sup> to the solid, and  $E_L$  the binding energy between all subsequent layers. The form of Eq. (10) is shown in Fig. 3, in which typical adsorption isotherms for various values of  $C$  are depicted. Generally,  $E_1 > E_L$ ,

<sup>2</sup> The prefix "ad" is used to imply involvement in the physical process of adsorption in an abbreviated way. Thus, "adlayer" is a layer of molecules adsorbed onto a surface and may be interchanged with "adsorbed molecular layer." Similarly, "admolecule" (used later) is an adsorbed molecule.

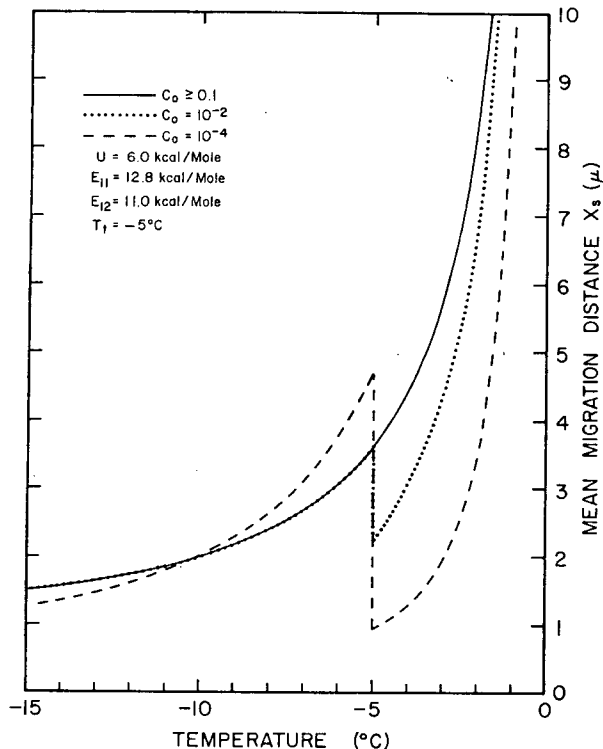


FIG. 5. The mean migration distance  $x_s$  as a function of temperature, calculated from Eq. (18) and normalized to a common value at  $-10^\circ\text{C}$  by adjustment of  $D_0$ .

so that  $C$  introduces a decreasing temperature dependence to  $n$  in Eq. (10). This temperature dependence will, however, be strongly countered by the tendency for  $X(T)$  to approach unity and therefore for the surface coverage to increase to many layers as  $P$  approaches  $P_L(T)$ . It is this second effect, arising from strong adsorbate-adsorbate interactions, which may be responsible for the tendency of all of the growth variables to increase with temperature. If for now we assume  $C_0 = 1$ , then for various values of  $\Delta E \equiv E_1 - E_L$  the dependence of  $n/n_m$  on temperature may be plotted as in Fig. 4. Even when the negative temperature coefficient introduced by  $C(T)$  is strong, its effect on  $n$  is always dominated near the melting point by the approach of  $X$  to unity.

#### b. The residence time $\tau$

In order to estimate the length of time that vapor molecules reside in the adsorbed layer, consider the equilibrium state and small deviations from it. At equilibrium, the desorption flux leaving the adlayer must just balance the adsorption flux entering the layer to maintain a given surface concentration. Now let the partial pressure of water vapor exceed the equilibrium value by an amount  $\delta P$  so as to increase the flux of molecules entering the layer by  $\beta\delta F$ , where  $\beta$  is a sticking or adsorption coefficient to account for impinging mole-

cules which are simply reflected. Since each of the additional vapor molecules which enters the adsorbed layer will, on the average, reside in the adsorbed state for a time  $\tau$  before it desorbs, the surface concentration will increase by an amount  $\delta n = \tau\beta\delta F$ . So,  $\tau$  may be calculated from the isotherm [Eq. (10)] using

$$\tau = \frac{\delta n}{\beta\delta F} = \frac{1}{\beta k_T} \frac{\delta n}{\delta P}, \quad (12)$$

to give

$$\tau = \frac{n_m C [1 + (C-1)X^2]}{\beta k_T P_L (1-X)^2 [1 + (C-1)X^2]}. \quad (13)$$

Particularly interesting is the term  $(1-X)$  in the denominator. In Eq. (13) [as in Eq. (10)] this term approaches zero as the temperature approaches the melting point. This means that, near that point, the residence time and the number of adsorbed molecules increase greatly.

To compare Eq. (13) with the expression for  $\tau$  used by others, note that if  $X$  is small,

$$\tau \approx \frac{n_m C}{\beta k_T P_L(T)} \approx \left( \frac{n_m C_0}{\beta k_T P_{L0}} \right) \exp(E_1/kT) \quad (14)$$

when the vapor pressure is written in the approximate exponential form,  $P_L = P_{L0} \exp(-E_L/kT)$ . Thus, for low surface coverages the temperature dependence of  $\tau$  is determined primarily by the energy  $E_1$  binding the first layer to the substrate and  $\tau$  has essentially the temperature dependence expected from the classical theory [Eq. (7)]. Since  $X$  is small at low temperatures,  $\tau$  will have the classical downward trend with increasing temperature until  $X$  attains an appreciable value, at which point the trend will be reversed. These results suggest that it may have been the assumed limitations to low surface coverage and no lateral interactions which have previously hindered the development of a more complete picture of the growth process.

It must be realized, however, that although the adsorbate-adsorbate interactions are responsible for the generally increasing residence times as the temperature approaches the melting point, the vapor molecules are adsorbed at all only by virtue of interactions with the underlying crystal. Hence, it is reasonable that the adsorption should be sensitive to the energy which bonds the first molecular layer to the solid even in the warmer region where adsorbate interactions dominate. The bonding directly to the solid might become weaker, for instance, if, indeed, a transition or reorientation of the molecules in the surface occurred. In this case, the number  $n$  and average residence time  $\tau$  of the adsorbed molecules would be expected to be reduced rather abruptly. On either side of the transition temperature the average trend upward would still be preserved,

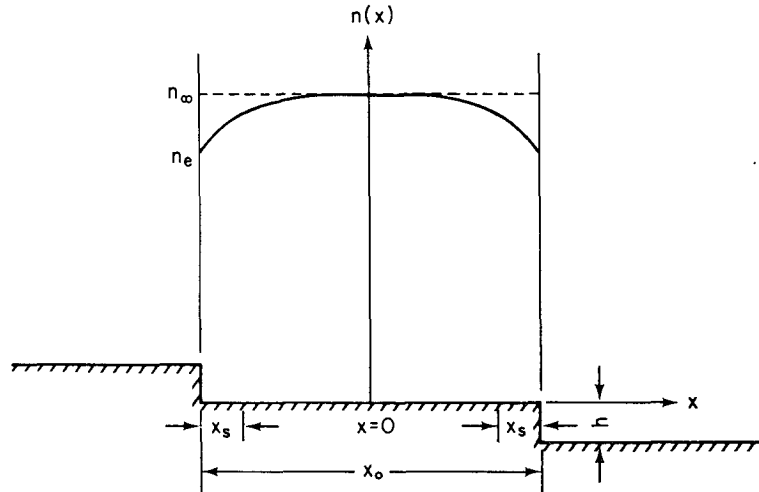


FIG. 6. The cross-sectional geometry of two parallel steps.

but a discontinuity in the growth parameters would be expected, perhaps giving rise to the observed maxima and minima.

To treat this idea quantitatively, allow the adsorbate-solid bonding energy  $E_1$  to take on different values above and below the transition. Thus, below the transition temperature  $T_t$ ,

$$C(T < T_t) = C_0 \exp[(E_{11} - E_L)/kT], \quad (16)$$

and above it,

$$C(T > T_t) = C_0 \exp[(E_{12} - E_L)/kT]. \quad (17)$$

The actual temperature at which the solid surface transition should take place is, of course, a function of the surface energy of the particular face, so the maxima and minima introduced into any growth parameter would be shifted relative to one another on the basal and prism faces.

*c. The mean migration distance  $x_s$*

Having now obtained an expression for the mean residence time and some insight into the possible origin of the quasi-discontinuity, we may use Eq. (5) to arrive at the final expression for the mean migration distance on the adsorbed multi-layer:

$$x_s^2(T) = \frac{n_m D_s C P_L [P_L^2 + (C-1)P_s^2]}{\beta k_T (P_L - P_s)^2 [P_L + (C-1)P_s^2]} \quad (18)$$

The magnitude of  $x_s(T)$  has been plotted in Fig. 5 for various values of  $C_0$ , the pre-exponential factor of the adsorption parameter  $C(T)$ , and using the two values of  $E_1$  specified by Eqs. (16) and (17). As indicated, both the trends of the curve and the magnitude of the discontinuity are portrayed realistically by the theoretical curves at least for small values of  $C_0$ . It is not expected, however, that the shift in the value of  $E_1$

would, in reality, occur as abruptly as has been assumed in the model, but to treat  $E_1$  in any other manner would presently be unjustified.

**4. Surface steps and the growth of ice**

*a. Step velocity*

In the last section the functional form of the mean migration distance  $x_s$  was derived without regard to the existence or behavior of steps on the surface. Here  $x_s$  will be used as an input parameter to treat the interactions of steps with one another and to determine their contribution to the linear growth rate of a face.

As was done by Hobbs and Scott (1965) let us consider the mass balance of adsorbed and migrating molecules on the surface, but with two differences: 1) there exists, in general, a finite (sometimes large) equilibrium concentration  $n_e$  of adsorbed molecules which serve no growth function, and 2) two parallel neighboring steps are allowed to interact by competing for the available excess of adsorbed molecules. The geometry for this development is that used by Strickland-Constable (1968) and is shown in Fig. 6. The  $x$  coordinate is taken perpendicular to the steps with the origin one-half the distance  $x_0$  between them. The concentration of excess admolecules  $\delta n$  is determined as a function of surface position  $x$  from the equation of molecular continuity, i.e., from

$$D_s \frac{d^2(\delta n)}{dx^2} - K_D \delta n + \beta \delta F = 0, \quad (19)$$

which simply accounts for the molecular fluxes due, respectively, to surface migration, desorption and adsorption. The assumption that the desorption flux is linearly proportional to the excess concentration  $\delta n$  is justified whenever the deviation from equilibrium is small. The proportionality constant  $K_D$  is the desorp-

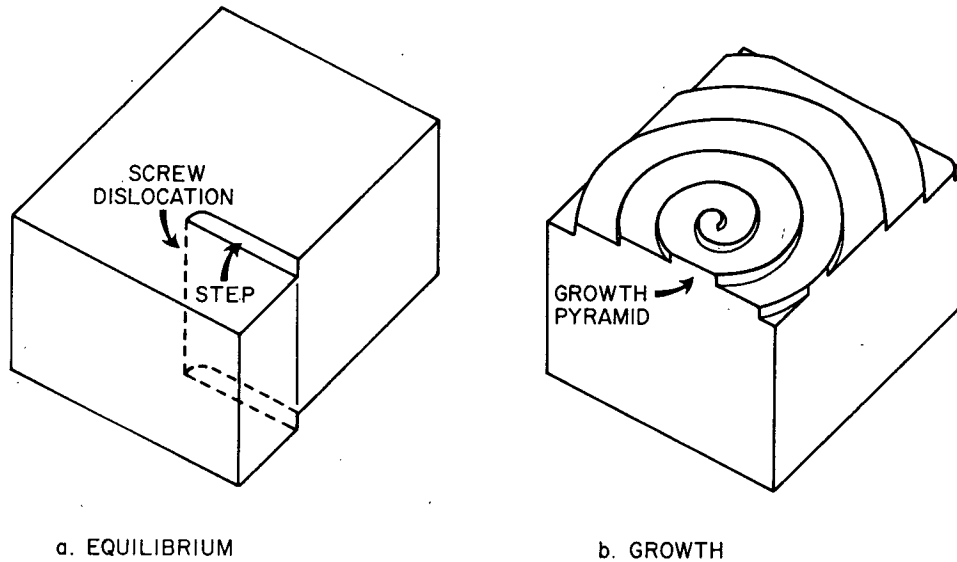


FIG. 7. The generation and growth of a step in a face by the emergence of a screw dislocation.

tion probability per unit time, the equivalent of the desorption constant used by Hobbs and Scott; it is the reciprocal of the residence time  $\tau$ .

Thus, from Eq. (5),  $K_D = 1/\tau = D_s/x_s^2$ , and the solution to Eq. (19) is

$$\delta n(x) = n(x) - n_e = \tau \beta \delta F \left[ 1 - \frac{\cosh(x/x_s)}{\cosh(x_0/2x_s)} \right], \quad (20)$$

which assumes that the outer boundaries are growing steps which act as infinitely good sinks for excess ad-molecules, i.e.,  $\delta n(\pm x_0/2) = 0$ .

Molecules diffuse to each step of height  $h$ , enter the step, and provide for its advance at a rate  $v$  given by

$$v = (2\Omega/h)x_s \beta \delta F \tanh(x_0/2x_s), \quad (21)$$

an expression which cares for the case of a limited fetch. Note that this expression degenerates to the simplified equation given by Hallett (1961) and by Hobbs and Scott when  $x_s \ll x_0$ . In general, however, each step will have neighboring steps which compete for the supply of adsorbed molecules so that the full expression [Eq. (21)] is necessary.

#### b. Step sources

The development leading to Eq. (21) gives an idea of how steps interact on a surface characterized by the parameter  $x_s$ , provided that the steps exist in the first place. Remember that, without a continual source of steps somewhere on the surface, steps will simply advance to the crystal edge and disappear, stopping further growth. This means that, since regeneration of steps by two-dimensional nucleation, with ensuent growth, is energetically improbable at the low supersaturations normally present during growth, a mecha-

nism other than two-dimensional nucleation must be responsible for the growth which is observed (Cabrera and Burton, 1949). The most likely mechanism is that first proposed by Frank (1949) and based upon the emergence of screw dislocations at the surface. This spiral step mechanism does seem to be the dominating mechanism of growth with some other substances (Bradley and Drury, 1959); also, observations have been made of spirals on crystalline faces of ice growing from the melt (Ketcham and Hobbs, 1968) and of curved trains of steps during vapor growth (Lamb and Scott, 1972). As seen schematically in Fig. 7a, when one part of the lattice is shifted relative to the other by a shearing action, a step will necessarily appear in the surface and have the important characteristic that it can never disappear as long as the screw dislocation continues to emerge on that face. Under conditions of equilibrium the step will be stationary and straight. In the presence of a supersaturated vapor, however, the step will advance and wrap itself up into a spiral about the dislocation, as seen in Fig. 7b. Following the treatment of Burton *et al.* (1951), we assume that the spiral has a stationary geometry which is approximately Archimedean such that the radius vector  $r$  from the dislocation is proportional to the angular distance  $\theta$  by

$$r(\theta) = \kappa \theta, \quad (22)$$

where  $\kappa$  is a temperature-dependent proportionality constant. The spacing  $x_0$  between steps is then

$$x_0 = 2\pi\kappa, \quad (23)$$

and the velocity  $v$  of steps far from the center of the spiral is

$$v = (2\Omega/h)x_s \beta \delta F \tanh(\pi\kappa/x_s). \quad (24)$$

### c. The linear growth rate

Obviously, for each full rotation of the spiral another step will be released from the center and allowed to propagate across the crystal face. The frequency  $f$  with which such steps are "generated" is

$$f = \frac{v}{2\pi\kappa}. \quad (25)$$

For a spiral step of height  $h$ , a new layer of crystalline material of thickness  $h$  is added to the growing face every time a step passes. Thus, the rate  $G$  at which a face advances parallel to itself is given by

$$G = fh, \quad (26)$$

or, using Eq. (25),

$$G = \frac{vh}{2\pi\kappa}. \quad (27)$$

The final dependence of the growth rate on the surface parameter  $x_s$  and the step shape factor  $\kappa$  is therefore

$$G = \Omega\beta\delta F(x_s/\pi\kappa) \tanh(\pi\kappa/x_s). \quad (28)$$

Of particular interest is the fact that this does not depend on the specific value of the step height or, therefore, on the magnitude of the displacement vector of the screw dislocation. The linear growth rate depends only upon the simple existence of a dislocation emerging at the surface with a screw component and upon the adsorption behavior of the water molecules. Also, although this treatment has been limited to a single step source, it is nevertheless general since it can be shown that the linear growth rate is governed solely by the single most active source on a face; the contributions to the growth from other, independent step sources is not additive (Strickland-Constable, 1968, p. 200). It is for this reason that a crystal face which is large compared to the mean migration distance may still maintain its relatively flat form even while growing in the presence of strong lateral gradients of excess pressure. Growth is strictly governed by the frequency at which steps pass a given point, this frequency being determined by conditions at the center of the most active spiral.

### d. The critical embryo

To complete this treatment, the temperature dependence of the spiral shape factor  $\kappa$  is required. This dependence is necessarily speculative since little is known about the actual behavior of steps in the immediate vicinity of the emerging dislocation core. Nevertheless, following the treatment of Burton *et al.*, we assume that the radius of curvature of the step can never be smaller than  $\rho^*$ , the radius of a critical two-dimensional embryo. This critical radius occurs at

the minimum radius of curvature (at  $\theta=0$ ) so that

$$\kappa = 2\rho^*. \quad (29)$$

If it is now assumed that molecular incorporation occurs at the steps by exchange with the adsorbed layer only, the temperature dependence of  $\rho^*$  can be found. First, consider a step without curvature. The molecular exchange which occurs between the step and the adsorbed state may be thought of as being comprised of a flux  $f_i$  of molecules continually entering the lattice at the step (and contributing to its advancement) and a flux  $f_0$  of molecules leaving the step (tending to retard the advancement). To a first approximation, the flux into the step is proportional to the concentration of molecules  $n_0$  directly in contact with the step:

$$f_i = b_i n_0, \quad (30)$$

where  $b_i$  is the proportionality factor. The flux leaving the solid surface at the step, on the other hand, is independent of  $n_0$  but is expected to be dependent on the temperature and the energy  $E_0$  required to remove a molecule from the lattice and place it in the adsorbed state. This is commonly expressed through the standard Arrhenius form

$$f_0 = A \exp(-E_0/kT), \quad (31)$$

where  $A$  is a configurational term and  $E_0$  the energy required to create the intermediate, activated state. At equilibrium, the incoming flux is just balanced by that outgoing, i.e.,

$$f_i = b_i n_e = f_0 = A \exp(-E_0/kT), \quad (32)$$

which implies

$$n_e = (A/b_i) \exp(-E_0/kT). \quad (33)$$

For any concentration greater than this equilibrium value the step will advance and wind up into a spiral having radii of curvature which continually decrease toward the center, the site of the emerging dislocation. But, because of the finite curvature, the activation energy at any point along the spiral, where the radius of curvature is  $\rho$  and the edge energy is  $\eta$ , will be reduced to

$$E_0' = E_0 - \frac{\eta a}{\rho}, \quad (34)$$

where  $a$  is the lattice spacing (see Burton *et al.*). Now, if a quasi-equilibrium is maintained, the concentration  $n_e$  of adsorbed molecules in close proximity to the curved step is, from Eq. (33),

$$n_e = (A/b_i) \exp\{[E_0 - (\eta a/\rho)]/kT\}, \quad (35)$$

or

$$n_e = n_e \exp(\eta a/\rho kT). \quad (36)$$

The exact center of the spiral does not grow because the high curvature prevents any net flux of molecules



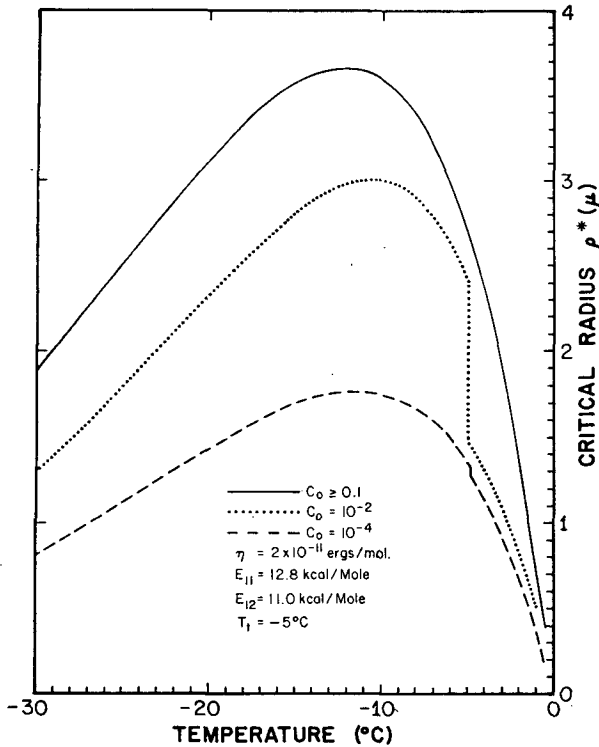


FIG. 8. The dependence of the critical radius  $\rho^*$  of a two-dimensional "pillbox" imbedded in an adsorbed multi-layer (for  $\delta P = 10 \mu\text{m Hg}$  or  $13.3 \mu\text{b}$  and the same normalization as Fig. 5).

from entering into the lattice. Hence, near that point there is no accumulation and, specifically, no diffusive term in Eq. (19). The concentration of adsorbed molecules near the spiral center should then just equal that concentration ( $n_\infty$ ) that would exist far from any steps:

$$n_\infty = n_e + \Delta n,$$

where

$$\Delta n = \frac{\beta \delta F}{K_D} \tag{37}$$

Hence,

$$n_e = n_e \exp(\eta a / \rho^* k T) = n_\infty,$$

and

$$\rho^* = \frac{\eta a}{k T \ln(n_\infty / n_e)} \tag{38}$$

or

$$\rho^* \approx \frac{\eta a}{k T} \frac{n_e}{\Delta n} \tag{39}$$

for small departures from equilibrium. Through the BET equations,  $n_e$  and  $\Delta n$  are functions of the saturation and excess pressures, so Eq. (39) can also be

written

$$\rho^* = \frac{\eta a}{k T} \left\{ \frac{(P_L - P_s)[P_L + (C - 1)P_s]}{P_L^2 + (C - 1)P_s^2} \right\} \frac{P_s}{\delta P} \tag{40}$$

which, when  $C = 1$ , reduces to the simpler expression

$$\rho^* = \frac{\eta a}{k T} \left( \frac{P_L - P_s}{P_L} \right) \frac{P_s}{\delta P} \tag{41}$$

Eqs. (40) and (41) predict an extraordinary temperature dependence for  $\rho^*$  (see Fig. 8). At the lower temperatures (below about  $-12^\circ\text{C}$ ) when  $P_L - P_s$  is increasing or constant with increasing temperature,  $\rho^*$  increases with increasing temperature in a manner predicted by classical theory. However, at the warm temperatures near  $0^\circ\text{C}$ , when  $P_L - P_s$  approaches zero,  $\rho^*$  decreases with increasing temperature. The effect is directly related to the number of adsorbed layers on the surface: when there are few adsorbed molecules, there is classical behavior; but, when many are present, nucleation effects are reversed. [It is interesting that Ownby (1972) and Sandejas and Hudson (1968) have found multi-layer adsorption during adsorption on metals, and at the same time, a marked decrease in the observed values of the critical supersaturation.]

*e. The condensation coefficient and the primary habits*

The general expression for  $G$  given in Eq. (28) may now be compared with  $G_{\text{max}}$  to obtain a value for the condensation coefficient  $\alpha$ , which, as defined earlier, is the probability of molecular incorporation. Eqs. (1) and (2) predict that

$$G = \alpha \Omega \delta F, \tag{42}$$

which, when compared with Eq. (28), indicates that

$$\alpha = \beta [(x_s / \pi \kappa) \tanh(\pi \kappa / x_s)], \tag{43}$$

or

$$\alpha = \beta \gamma, \tag{44}$$

where

$$\gamma \equiv (x_s / \pi \kappa) \tanh(\pi \kappa / x_s) \leq 1 \tag{45}$$

may be termed the "incorporation" coefficient and  $\kappa$  is given by Eqs. (29) and (40). The overall "condensation" coefficient  $\alpha$  may be viewed as composed of two components; a "sticking" coefficient  $\beta$  which accounts for impinging vapor molecules which never even become adsorbed, and the "incorporation" coefficient  $\gamma$  which gives the fraction of adsorbed molecules which actually make it into the lattice structure. Although real measurements of linear growth rates are incapable of resolving the condensation coefficient into its components, it is obvious that neither component can be smaller than the measured value  $\alpha$ . Until further evidence becomes available the sticking coefficient  $\beta$  must remain unknown and will be set equal to unity in this treatment.

The incorporation coefficient  $\gamma$  is, on the other hand, a well-defined function of the ratio  $x_s/\pi\kappa$  [ $=2x_s/x_0$ ] arising from the model and is shown in Fig. 9. When twice the mean migration distance ( $2x_s$ ) is small compared to the step spacing  $x_0$ , the probability that an impinging vapor molecule will incorporate is also small and proportional to  $x_s$ . In this regime the assumption that  $\gamma=1$  within the catchment distance  $x_s$  from each step, and zero elsewhere, is valid. However, as  $2x_s$  and  $x_0$  become comparable in magnitude this assumption breaks down. In the extreme, when  $x_0 \ll 2x_s$ , the relative size of the two quantities is of no significance because the surface becomes saturated with steps and all adsorbed molecules become incorporated without desorbing; the condensation coefficient  $\alpha$  becomes limited solely by the value of the sticking coefficient  $\beta$ .

With the temperature dependence of the spiral shape factor  $\kappa$  now available, it is possible, via Eqs. (45), (40) and (29), to calculate the dependence of the incorporation coefficient  $\gamma$  on temperature. This important result is shown in Fig. 10 for a surface transition at  $-5^\circ\text{C}$  and three values of the adsorption parameter  $C_0$ . It is apparent that the change of the surface binding energy  $E_1$  has an appreciable effect at small values of  $C_0$ .

As a final presentation of the theoretical results, the linear growth rate measurements of Lamb and Scott and the step interaction distance measurements of Mason *et al.*, are used to choose a set of model parameters which provide for a reasonable agreement between theory and experiment. The resulting trends to the probabilities of molecular incorporation on the basal and prism faces of ice are shown in Fig. 11. The imposed discontinuities in the binding energies on the two faces clearly show how an alternation in the primary crystal habit may arise. This model of surface effects and multi-layer adsorption presents a plausible explanation for the observed variations of ice crystal habits with temperature.

5. Summary and conclusions

In this paper we have considered the effects of multi-layer adsorption of water vapor on the basal and

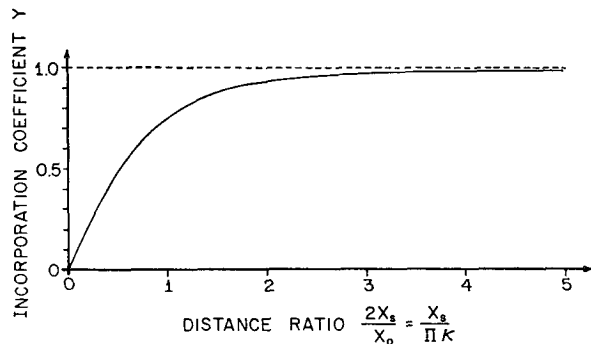


FIG. 9. The dependence of the incorporation coefficient  $\gamma$  on the dimensionless distance ratio  $2x_s/x_0$ .

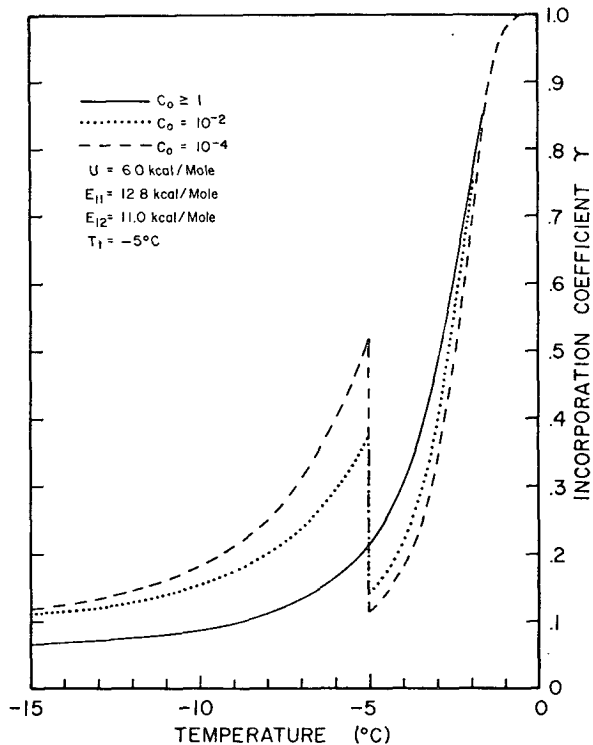


FIG. 10. The dependence of the incorporation coefficient  $\gamma$  on the temperature, the surface binding energy  $E_1$ , and  $C_0$  (same normalization as Fig. 5).

prism faces of ice. It appears that, because of the significant attractions such adsorbed molecules may have for one another as the condensation point is reached, their residence times on the surface increase greatly and the molecules migrate long distances. Steps growing on the surface are therefore able to gather adsorbed molecules from larger distances and, as a result, they propagate faster. In addition, the spacing between steps of a spiral originating from the emergence of a screw dislocation is dependent on the magnitude of the minimum radius of curvature which decreases with increasing temperature due to a large increase in the supersaturation of adsorbed molecules on the surface. The net effect of the increased rotation rate and the narrower step spacing is a tendency for the linear growth rate to increase dramatically as the temperature approaches the melting point. This upward trend is countered, however, by the competition of the steps for the available excess adsorbed molecules, causing the condensation coefficient to approach unity at the melting point. Superimposed on this average increase with temperature is the possibility of an independent phenomenon above a certain temperature: a surface disordering which reduces the bonding of the adsorbed molecules to the surface. A relatively abrupt reduction in the surface concentration of adsorbed molecules results in a reduction in the residence time and the magnitudes of all growth variables. Such a

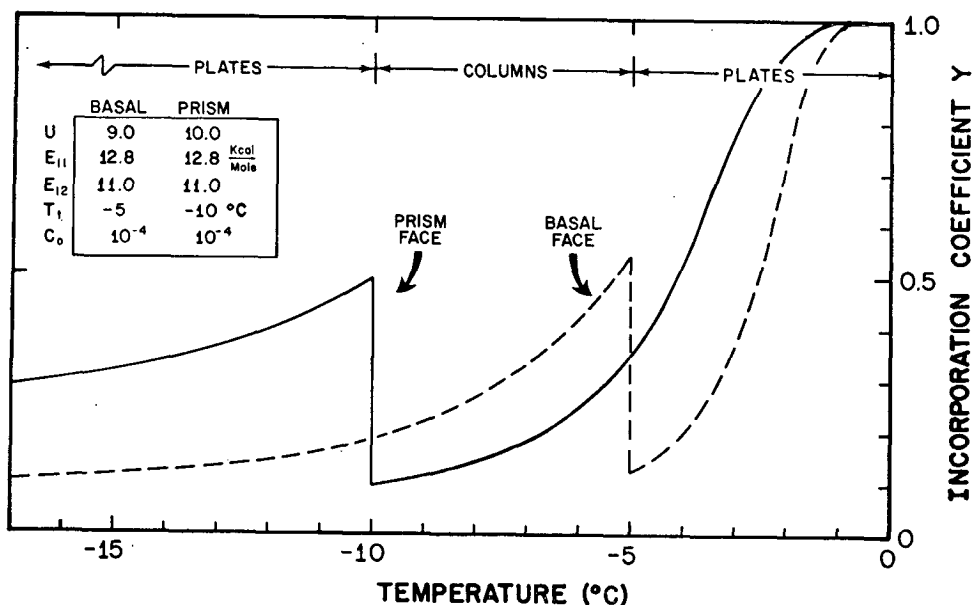


FIG. 11. The predicted trends to the incorporation coefficients and primary habits of ice for the indicated values of the parameters.

basic mechanism of growth on both the basal and the prism faces of ice can explain the peculiar alternation of the primary habit with temperature.

In order to arrive at a theoretical expression for the rate of growth of ice and to provide a mechanism for the formation of the primary habits, interactions between adsorbed water molecules which led to multi-layer adsorption were considered. The BET adsorption model has been used, in conjunction with the theory of Burton *et al.* (1951) in order to develop a quantitative treatment. The intention has been to present a specific hypothesis that is consistent with the observations. Hence, before the present treatment is applied, the adsorption model and the growth mechanism may need some revisions.

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