PROGRESS IN CRYSTAL-GROWTH THEORY

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ABSTRACT

The purpose of this paper is to trace the progress that has been made in the theories of crystal growth and to suggest that reaction-rate theory might be necessary for a full understanding. Consideration is given to (a) the role of thermodynamics in the equilibrium shape of crystals, (b) measurements of surface diffusion of molecules, (c) measurements of interfacial free energy, (d) the shape as a function of rate of growth, (e) the effect of solvent upon shape, and (f) the difference in growth rate of asymmetrical crystals in opposing directions. Activation energies are applied to the process of dissociation of wrongly attached molecules before they can become free to reattach correctly.

SOMMAIRE

Nous voulons ici faire le bilan des progrès faits en théorie de croissance cristalline et montrer que la théorie des vitesses de réaction sera probablement nécessaire pour bien comprendre le phénomène. Nous prenons en considération: (a) le rôle de la thermodynamique dans la forme d'équilibre des cristaux, (b) les mesures de la diffusion de surface des molécules, (c) les mesures d'énergie libre aux surfaces de contact, (d) le faciès en fonction des vitesses de croissance, (e) l'effet du solvant sur le faciès et (f) la différence entre les vitesses de croissance dans les deux sens opposés d'une direction polaire d'un cristal. Nous appliquons des énergies d'activation au processus de dissociation de molécules attachées en mauvaise orientation, afin qu'elles puissent se libérer et s'attacher correctement.

(Traduit par la Rédaction)

INTRODUCTION

This paper reviews the contributions of past researchers to crystal-growth theory, but by no means does it cover all the important work in the field. For a more detailed history of crystal growth and crystal morphology the reader is referred to books by Phillips (1946), Buckley (1951) and Schneer (1977). After describing some experiments on surface migration of molecules, surface free energy, means of measuring growth rates and effect of choice of solvent upon crystal shapes, a suggestion is made that perhaps the process of crystal growth is a reaction-rate phenomenon. To use this suggestion the researcher is faced with the problem of making measurements for which laboratory techniques are not known and applying a statistical-mechanical mathematical approach that is very complicated.

SOME OF THE EARLIER WORK

To introduce a discussion of the mechanism of growth of crystals we should consider some early contributions by authors interested in the morphology and general shape of crystals (Phillips 1946). One of the first generalizations was the law of constancy of angles by Nicholaus Steno who in 1671 said, in effect, that regardless of the shape or size of a crystal of a given species, the angles between the respective faces are the same. Then René Just Haüy (1784) showed through beautiful and intricate drawings how a crystal could be built by stacking together identical blocks to form solids (Phillips 1946) having flat faces that were not necessarily parallel to the faces of the initial building blocks. This work no doubt helped to convey the idea of unit cells and Miller indices which later became so essential in the determination of crystal structures by use of X-ray diffraction.

THERMODYNAMICS

Virtually no application of thermodynamics to crystal morphology was made until Gibbs (1875) wrote the equation

$$a_1\gamma_1 + a_2\gamma_2 + a_3\gamma_3 \ldots . \text{ tends to a minimum} \quad (1)$$

$$i.e., \ \sum_1^n a_j \gamma_j \ \text{ tends to a minimum} \quad (2)$$

where the subscripts j are arbitrary numbers assigned to each of the n faces of the crystal, a_j is the area of the j face and γ_j is the free energy per unit area of the face.

Equation (2) can be modified to cover the case where there are m crystals of varying size in the solution (not just one):

$$\sum_{1}^{m} \left(\sum_{1}^{n} a_{ij}\,\gamma_j \right) \text{ tends to a minimum} \qquad (3)$$

where i is an arbitrary number assigned to each of the m crystals and a_{ij} is the area of the ith face of the jth crystal. Equation (3) suggests that in a solution in equilibrium with many crystals of differing sizes, the large ones should grow at the expense of the smaller ones until only one large crystal is left. The test of equation (3) has inspired much work on the measurement of the solubility of crystals as a function of size, beginning with Hulett (1901, 1905). Meanwhile, Ostwald (1900) was deriving mathematical equations to fit the data. Buckley (1951) describes in English the work of many researchers whose general conclusions conform to equation (3).

However, the problem takes on a different aspect when dealing with crystals smaller than the critical nuclear size. Hirth & Pound (1963) discuss nucleation in depth and consider the equation,

$$\triangle G = 4\pi r^2\,\delta \;+\; \frac{4}{3}\,\pi\,r^3\,\triangle G_v \qquad (4)$$

where r is the radius of the particle, δ is the interfacial free energy of the particle per unit area and $\triangle G_v$ is the free energy of the particle per unit volume. As $\triangle G_v$ is negative, a plot of $\triangle G$ vs. r produces a curve showing a maximum for $\triangle G$ at a certain value of r which we call r_c or critical radius. Only crystals much larger than r_c are to be considered here because smaller aggregates are unstable.

Curie (1885) postulated that if one located a position inside the crystal at which the crystal started growing and drew vectors out from this point perpendicular to each of its faces, the length h_j measured could be divided by the surface free energy to give a constant for all faces measured:

$$\frac{h_1}{\gamma_1} = \frac{h_2}{\gamma_2} = \frac{h_3}{\gamma_3} = \frac{h_4}{\gamma_4} = \text{a constant} \qquad (5)$$

This became known later as the Wulff theorem (Hilton 1903) when Wulff (1901) took up the matter and constructed polar graphs to represent the principle. Examples of these charts have been published by van Hook (1961) and by Strickland-Constable (1968) and treated in a rigorous manner by von Laue (1943). An English translation of von Laue's work was made available through Schneer (1977).

On the application of statistical mechanics to crystal growth, some interesting examples were given for the roughness of crystal surfaces by

Burton et al. (1951) and Jackson (1958a). These authors showed that the equilibrium between a crystal face and a saturated solution is similar to the problem of miscibility gaps in solid solutions of metal alloys, as taught by Gordon (1968) and Prince (1966).

GENERAL RULES

Since 1840, a number of related conclusions have been derived on the basis of observation. One of the most interesting was the law of Bravais (1850): for any crystalline species a translation lattice can be found such that (1) the observed crystal faces are parallel to the net planes with the highest reticular density (or smallest mesh areas), and (2) the greater the reticular density (or smaller the mesh area) the more important the corresponding form. Much confirmatory work was performed between 1904 and 1926 by Friedel (1905). Much later Donnay & Harker (1937) wrote a paper that did much to renew interest in crystal morphology; they extended the law of Bravais by considering screw axes and glide planes. McLachlan (1952) tried to extend the Donnay-Harker law by using a theory of laminarity. Schneer (1970) showed that an approximation of the crystal structure of barite could be obtained by use of the dominance of forms instead of structure factors.

SOME RECENT EXPERIMENTS

Like many researchers in the past, the present author and colleagues were impressed by the fact that there are no adequate means for making all the measurements necessary for testing existing crystal-growth theories or developing new ones. For the present study, α–resorcinol was chosen for measurements because it represents a general example of anisotropic crystal growth: it can be considered as a polar molecule (Fig. 1) and forms a polar crystal as shown in Figure 2 (Winchell 1943). The structure of re-
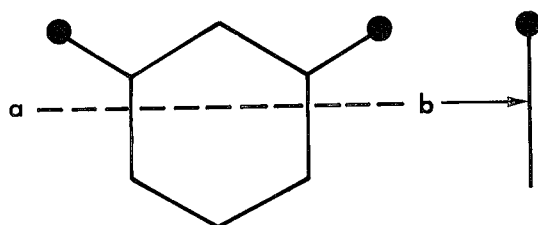

FIG. 1. (a) The resorcinol molecule drawn to show its polarity. The black dot represents the hydroxyl group. (b) Schematic representation of a polar molecule. The black dot represents the hydrophylic end and the stem represents the hydrophobic end.
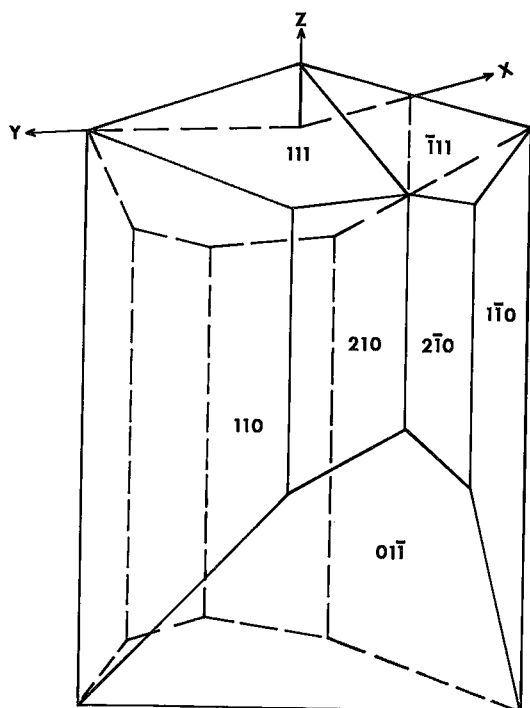
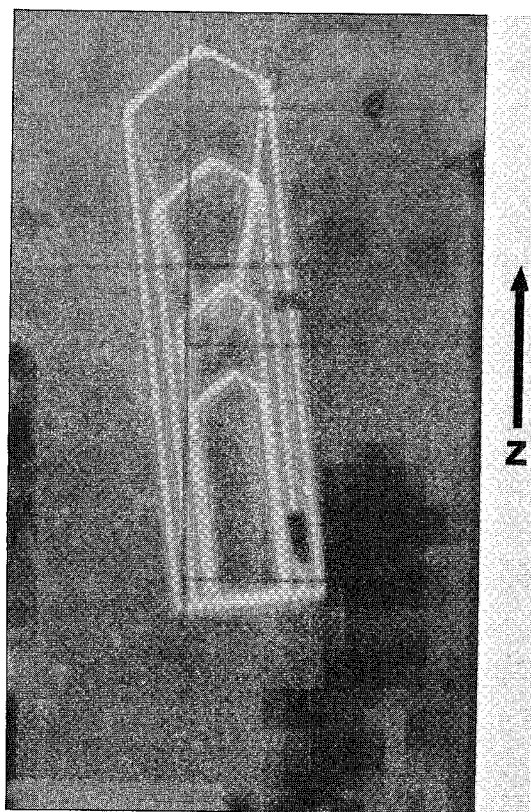FIG. 2. The morphology of the α-resorcinol crystal.

FIG. 3. Four stages in the growth of a thin resorcinol crystal (Cox & McLachlan 1974) The Z axis is vertical. By permission of the *Journal of Crystal Growth*.

sorcinol belongs to the non-centrosymmetrical space group C^9_{2v} *(Pma)* (Robertson 1936). It is impossible to imagine a crystal growing to the shape shown in Figure 2 without growing at different velocity in the plus z direction than in the minus z direction. The non-equivalence of rates of growth in opposing directions of growth is not to be considered as rare: 21 of the 32 point groups are non-centrosymmetrical.

In order to measure the rate of growth of resorcinol, a schlieren-type microscope was built by Cox & McLachlan (1974). Figure 3 shows four stages of growth taken at one-minute intervals. Note that the growth in the positive z direction is much faster than in the minus z direction. By enlarging Figure 3 and making a scale model as shown in Figure 4 we find h values referred to in equation (5): the growth rate of the {011} face is 1.3×10^{-2} cm/min., whereas the {010} plane grows at 2.3×10^{-3} cm/min., or about one-sixth as fast. In comparison, the growth rate in the minus z direction is almost zero.

Before continuing discussion of measurements, it is well to make distinctions between the following shapes of crystals and to indicate the branch of science pertaining to each: (A) Equilibrium shape: thermodynamics; (B) Steady-state shape: reaction-rate theory; (C) Transient growth: irreversible thermodynamics.

(A) The equilibrium shape of a crystal is not really associated with the growth of a crystal but rather represents its shape when the crystal has equilibrated with the saturated solution after growth. If we knew the equilibrium shape we could test equation (1) of Gibbs (1875) and the theorem of Wulff (1901) expressed by equation (5). Assuming that the equilibrium shape is that obtained at infinitely slow rates of growth, experiments were performed on resorcinol (Cox 1971) which resulted in Figure 5. As the z axis was still shrinking relative to the other axes at the slow rate of cooling of 0.1°C per nine days, we gave up the idea of finding the equilibrium shape.

In applying equations (1) and (5), the surface energies γ_j need to be measured. One method of measuring the free energy of the solid–liquid interface has been applied commonly in the study of ore dressing (Taggart *et al.* 1930). This
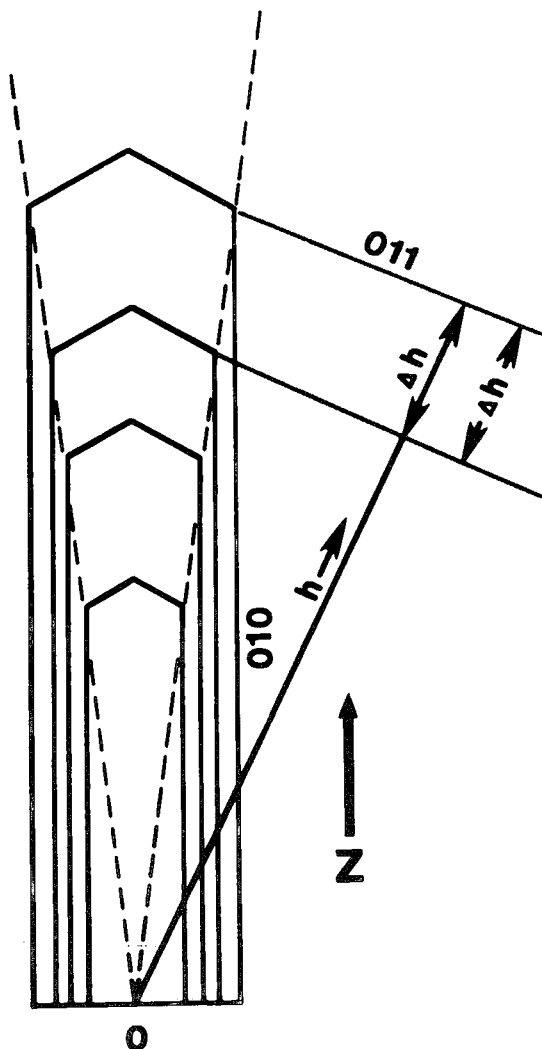
FIG. 4. A scale drawing of Figure 3 indicating that the crystal essentially maintained its shape.

procedure is called the sessile-drop method. A drop of liquid is deposited on a solid surface as shown in Figure 6, and the first step is to measure the contact angle Θ. As the sessile-drop method permits evaporation of the solvent and thereby an increase in concentration of the solute, an apparatus was built by McLachlan & Cox (1975) to measure the contact angle between a bubble of air and the crystal surface while the crystal is submerged in a saturated solution, as shown in Figures 7a and b. The equation to be used is the same as that used for the sessile drop (cf., Figs. 6a & b):

$$\gamma_{SV} = \gamma_{LV} \cos\Theta + \gamma_{SL} \qquad (6)$$
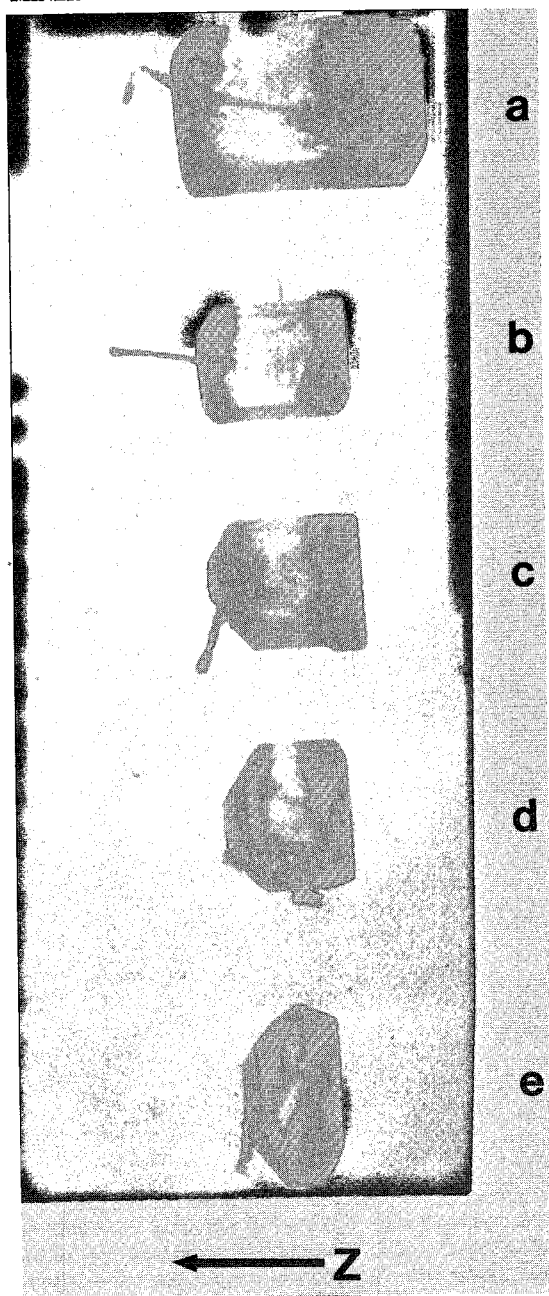
FIG. 5. (a) Resorcinol grown from water solution by temperature decrease of 2.5°C per day for one day; (b) grown by temperature decrease of 1.0°C per day for one day; (c) grown by temperature decrease of 0.5°C per day for two days; (d) grown by temperature decrease of 0.2°C per day for three days, and (e) grown by temperature decrease of 0.1°C per day for nine days.

where γ_{SL} is the surface free energy of the solid–liquid interface, γ_{SV} that of the solid–
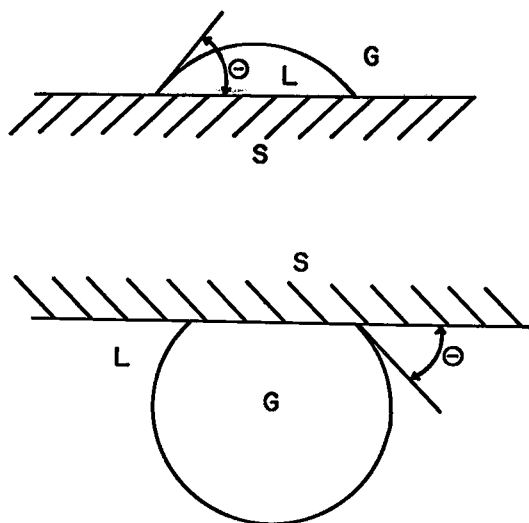
FIG. 6. Measuring interfacial free energy: above, the sessile drop with liquid on the solid in air; below, a bubble of air under the solid in liquid.

vapor interface, γ_{LV} that of the liquid–vapor interface and Θ the angle of contact. Choosing a well-formed resorcinol crystal and leaving it in a saturated solution for a reasonable length of time, it was found that γ_{SL} was zero on all faces. Only when the solution was undersaturated or supersaturated did non-zero values of γ_{LS} appear. In view of these findings and the great difficulty in getting the lower surface of the crystal sufficiently level to prevent the bubble from rolling off, the study of equilibrium was abandoned.

(B) The steady-state shape of a growing crystal is the main problem treated in this paper. Steady-state growth is associated with an increase in size of crystal without a change in shape. Two crystals have the same shape when the ratio of the areas of pairs of respective faces is constant during growth. This requires that each corner of a crystal during growth progresses outward from the origin in a straight line as in Figure 8. Inspection of Figures 3 and 4 indicates that resorcinol grew at a nearly steady rate.

(C) Transient growth is characterized by (1) dendritic crystals having tree-like or fern-like protrusions into the solvent from the corners e.g., ammonium chloride in an aqueous solution; (2) fins growing from edges and finally filling in to produce hopper crystals e.g., bismuth, or (3) a general roughness of faces without well-defined faces. These features are associated with growth from supersaturated solutions or supercooled melts.
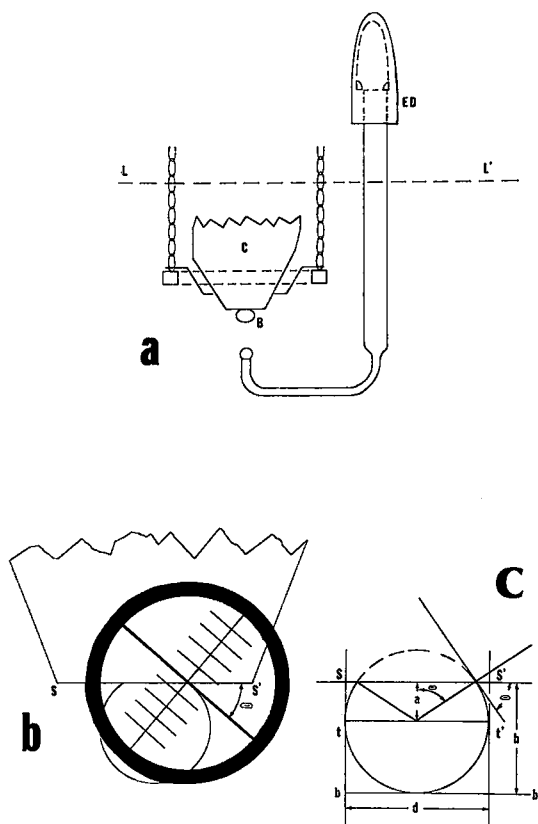

FIG. 7. (a) A modified eye dropper for depositing a bubble, B, of air on the underside of a crystal, C, where L-L' is the liquid level of the solution. (b) and (c) Two schemes for measuring the contact angle, Θ. After McLachlan & Cox (1975) with permission of Review of Scientific Instruments.

Because of the nature of the solubility curves of certain materials, it may be difficult for the investigator to control the concentration of the solute. For example, Figure 9 shows the water solubility of NH_4Cl as compared with that of $NaCl$. If we express the difficulty D of controlling concentration by the equation

$$D = \frac{1}{c} \frac{dc}{dT} = \frac{d \ln c}{dT} \qquad (7)$$

where C is the concentration in wt.% and T is temperature, we find that the D value of NH_4Cl is 7.8×10^{-3} deg.$^{-1}$ whereas that of $NaCl$ is 5.016×10^{-4}; NH_4Cl is almost sixteen times as prone to form a non-steady state crystal or dendrite as is $NaCl$. Figure 10 shows the effect of changing solvent while using the same compound, resorcinol. The D value of resorcinol in water is 1.19×10^{-2} deg.$^{-1}$ and in ben-
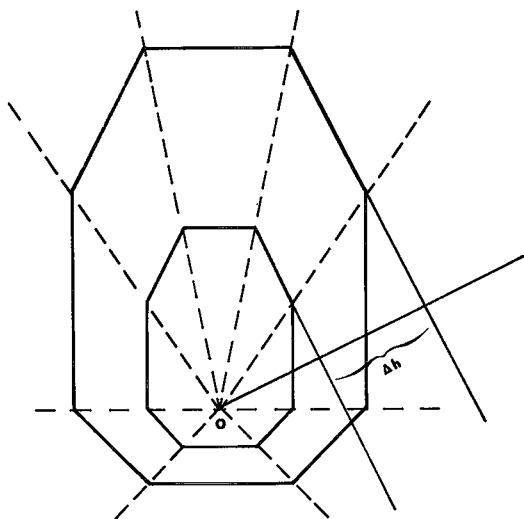
FIG. 8. A schematic drawing of two stages in the growth of a crystal that underwent steady-state growth. Note that lines drawn from the center, O, through consecutive corners are straight lines.
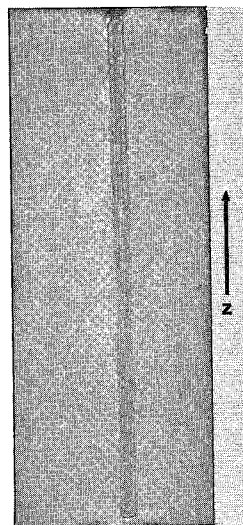
FIG. 11. A needle of resorcinol grown in benzene.
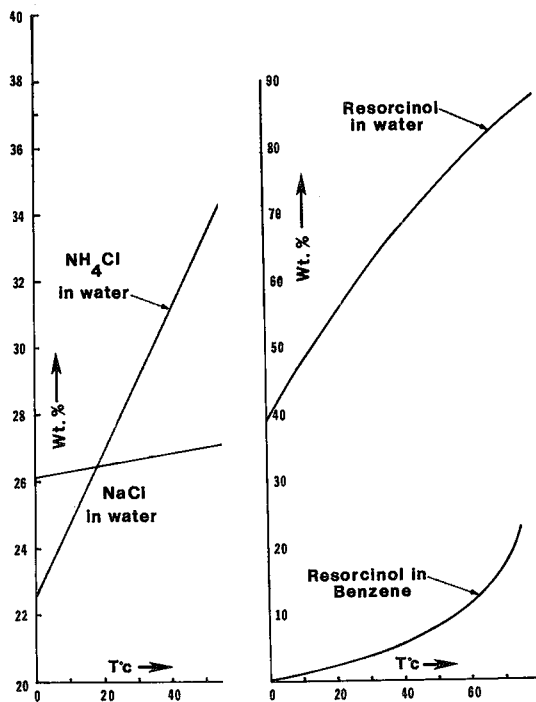
FIGS. 9. The solubilities of NH₄Cl and NaCl in water as a function of temperature. 10. The solubility of resorcinol in water and in benzene as a function of temperature.
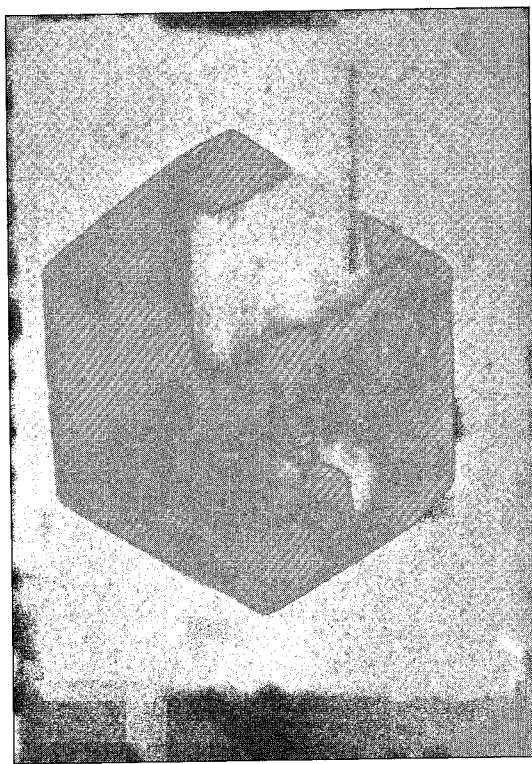
FIG. 12. A crystal of resorcinol grown in water using a small needle as seed: the needle had grown in benzene.

zene $9 \times {}^{2}10$; large faces are thus 7.5 times easier to form in water solutions as from benzene solution. In aqueous solution the crystals

FIG. 13. A large crystal of resorcinol grown in water was placed in saturated benzene solution and left to continue its growth. Note that the spines on the $+ Z$ end have the habit of crystals grown in benzene.

TABLE 1. THE ENTROPY OF MELTING OF METALS

ΔS_m of elements with simple structures

cubic close packed		hexagonal close packed		cubic body centred	
Ag	2.19	Ca	1.98	Cr	2.16
Au	2.21	Mg	2.34	Ba	1.83
Ca	1.98	Ni	2.43	Nb	1.76
Co	2.08	Pr	2.24	Mo	2.3
Cu	2.29	Zn	2.30	V	1.79
Pb	2.04	Ti	1.76*	Zr	1.76
Pt	2.30	Cd	2.46	Tl	1.79

ΔS_m of elements with complex structures

orthorhombic structure		diamond structure		arsenic structure	
Ga*	4.42	Si*	5.57	As	6.07
Br*	9.70	Ge*	6.74	Sb*	5.28
I*	9.43	Sn	3.40	Bi*	4.60

* observations of Jackson (1958). ΔS_m in entropy units.
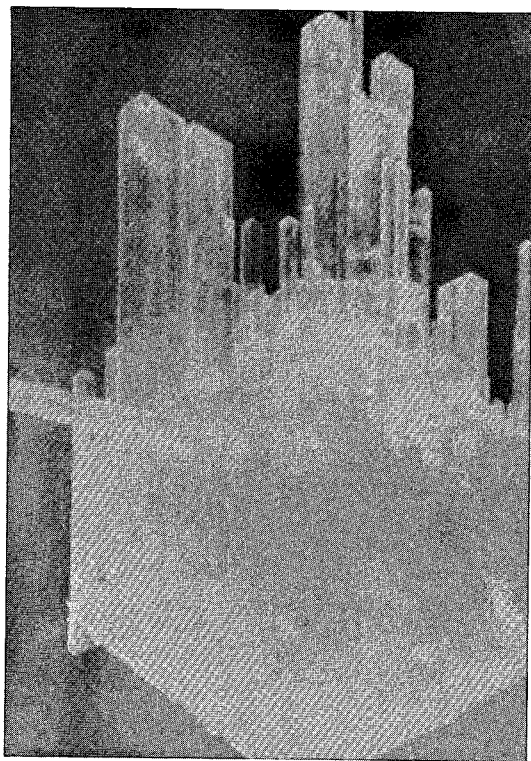
faces without distinct faces, might have to do with the entropy change in going from solution to crystalline solid. For metals grown from the melt, Jackson (1958b) proposed that in addition to entropy, the number of nearest neighbors influenced the roughness of crystals. In Table 1, the general structures of metals according to Wyckoff (1951) are divided into simple and complex structures. Entropies of fusion are obtained by dividing the heats of fusion by the temperatures of fusion as supplied by Gschneidner (1964). It is to be noted that simple structures have an entropy of melting in the neighborhood of two whereas complex structures have entropy changes exceeding four. The elements considered by Jackson (1958a), marked with a star, are among the complex structures listed in Table 1.

Although there are reasons for accepting the idea that entropy has an influence on the roughness of crystal faces grown from solution and from the melt, it is difficult to verify this because of absence in the literature of data on heats of solution necessary to get the entropy from $\Delta H / T$. Such authors as Bichowsky & Rossini (1936) and more recent sources such as the Bureau of Standards compilations furnish heats of solution that are not taken under equilibrium conditions, i.e., at saturation.

SURFACE MIGRATION

In view of the determination of a crystal to maintain a given shape while growing under steady-state conditions or to change to that characteristic shape, regardless of the shape of the seed or modifications due to grinding, one wonders about the mechanism by which these changes come about. Many theorists, including Stirling Hendricks (priv. comm. 1957), have

grow with large faces (Fig. 5), in contrast to the needle-like or lath-like crystals grown in benzene (Fig. 11). These and other pictures taken of resorcinol crystals grown in toluene, acetone, the alcohols, etc., demonstrate that crystal shape is a function of solvent. It has been shown that regardless of the shape of the seed from which a crystal is grown, the shape progressively changes to the shape characteristic of the solvent, even if the original seed is a polished sphere (Buckley 1951). Figure 12 shows a crystal of resorcinol grown in aqueous solution from a small needle-like seed grown in benzene. It has attained the shape characteristic of resorcinol grown in water; Figure 13 shows the result of using a large water-grown crystal as seed for growth in benzene solution. We suspect that these lath-like spines would eventually fill in to form a large but long crystal characteristic of that grown in benzene solution.

The shape of crystals, whether dendritic, hopper-shaped or merely exhibiting rough sur-
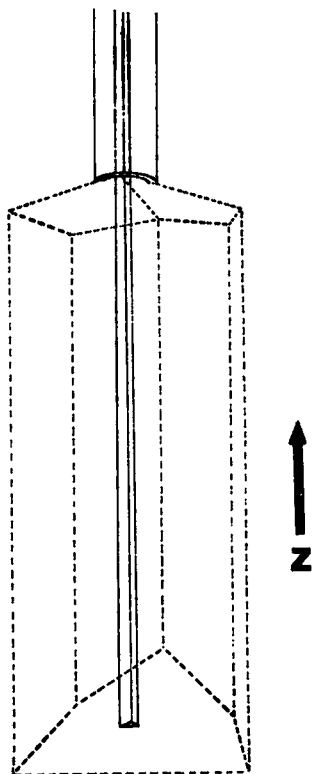
FIG. 14. A needle of resorcinol grown in benzene was placed in a glass capillary to continue its growth in an aqueous solution. Note that the crystal did not grow inside the capillary.

suggested that surface migrations of atoms or molecules might play a role. Cox (1971) performed the following experiments to check this possibility. A needle-like crystal of resorcinol (such as shown in Fig. 11) grown from a benzene solution was placed inside a glass capillary tube with a small portion of about 0.5 cm outside the capillary. This assemblage was placed in a saturated water solution of resorcinol and the crystal allowed to grow by gentle lowering of the temperature. The solid lines in Figure 14 show the capillary and the original crystal; the dotted lines show the crystal at the end of the experiment. The part of the crystal exposed to the water solution grew toward the shape characteristic of the solution, but the portion inside the capillary did not grow noticeably. If surface diffusion had been contributing to the shape, then the capillary should have been filled. This suggests that surface migration of molecules contributes very little to the habit of resorcinol crystal grown in water. Appropriate experiments also showed that surface diffu-

sion is not a significant factor for crystals grown in benzene.

MOLECULAR DIFFUSION FROM THE BULK OF THE SOLUTION

If we cannot accept surface diffusion to account for crystal shape, we are forced to consider the diffusion of molecules from the solution to the crystal faces as indicated in Figures 15a and b (see McLachlan & Carlson 1952), where the dotted lines represent the paths of diffusion and solid lines represent equiconcentration contours. Note that at the acute corner in Figure 15a, the flow lines are more concentrated than at the faces, and the concentration contours are closer together, while at the obtuse corner in Figure 15b, the flow lines are far apart. As growth continues, the acute angles get progressively more acute and dendritic growth is to be expected. Vogel (1921)
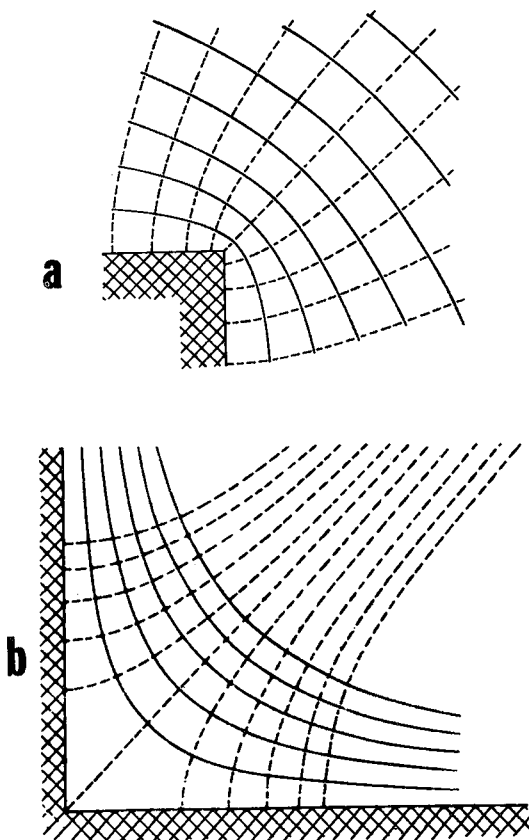

FIG. 15. (a) The flow lines and equiconcentration lines of solute at and near a protruding corner of a crystal; (b) the similar effect at and near a receding corner of a crystal.

and others have considered this matter; experimental determinations of concentration gradients in the solution near the edges and surfaces of crystals have been made by Berg (1938) and later by Bunn (1949) which document this phenomenon. The flow of heat to or from the crystal was also considered by Vogel (1921). The theoretical treatment of this effect falls into the category of field theory (Smythe 1939) and as suggested by McLachlan & Carlson (1952), should be treated by "conformal mapping" to which Walker (1933) applied the mathematics of fluid flow, heat flow and electrostatics. Unfortunately, the Schwartz-Christoffel equations that are used in field theory in general apply only to two dimensions and therefore only to *edges* of crystals and not to the corners where some of the more interesting dendrites originate. Nevertheless one can see that concentration-sensitive materials such as NH_4Cl (in water) and resorcinol (in benzene) are more susceptible to fast diffusion at edges and corners and therefore to variable growth rates.

REACTION RATES

There is one problem which confronts any theorist who considers the growth of crystals that belong to any one of the twenty-one point groups that have no centre of symmetry; that is, the $\{hkl\}$ faces do not all grow at the same rate as the corresponding $\{\overline{hkl}\}$ faces. The idea that the faces of greatest area are those having the largest d spacings falls short of distinguishing the differing rates of growth in opposite directions, because the d spacing is the same regardless of whether it is measured in the plus direction or the minus direction. This renders the law of Bravais and the Donnay–Harker law inapplicable to noncentrosymmetric crystals and the laminarity theory of McLachlan is inadequate also. In steady-state rates of growth we now turn to reaction-rate theory (Glasstone *et al.* 1941).

Consider a water solution of polar molecules, each having a hydrophobic part and a hydrophylic part (Fig. 1) bathing a polar crystal shown schematically in Figure 16, inside the dotted lines *a-b-c-d*. The polar molecules are arranged (head-to-tail) in the crystal in a north-south direction. We can imagine that in the solution the polar molecules can be associated with water molecules by having water attached to either head or tail. Of course hydrogen bonding stipulates that the water is much more strongly attached energetically to the hydrophylic (or head) end than to the hydrophobic
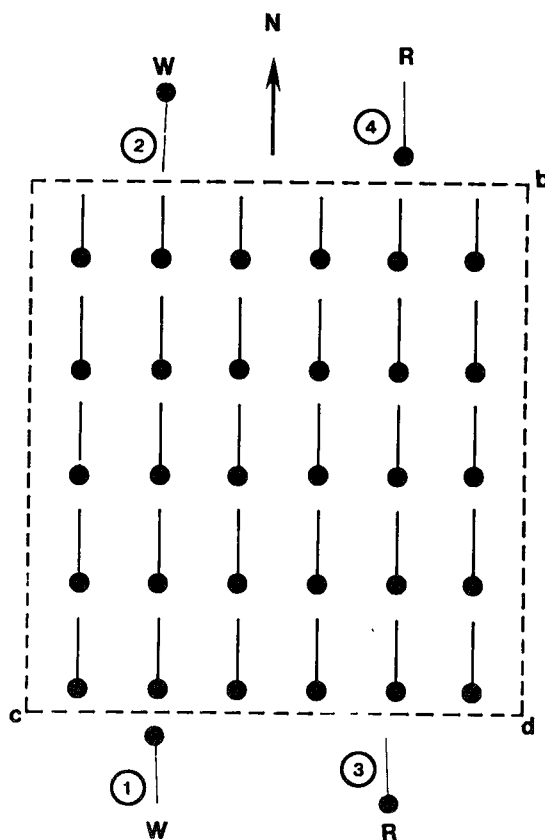
FIG. 16. An assemblage of polar molecules arranged to represent the structures of a polar crystal, with attached molecules at positions (1), (2), (3) and (4).

end. Also, some of the molecules in solution can be attached to one another head-to-head, tail-to-tail or head-to-tail with again differing energies of attachment. On the surface of the crystal in Figure 16 two molecules, (1) and (2), are illustrated in the wrong position where they prevent continued growth of these surfaces while maintaining the polar character of the crystal. Molecules (3) and (4) are in the correct position and can remain. The energy required to remove molecule (1) so that another molecule can arrive there is greater than that for molecule (2).

As the various energies of bonding and the concentrations of clusters are not known or measurable we can illustrate our lines of reasoning by following an oversimplified process. Consider an average isolated or free polar molecule having an energy E_f as shown at position a in Figure 17. From this free condition it could diffuse to the wrong position (2) of Fig-

FIG. 17. An energy level diagram with the usual "reaction" coordinate. Starting on the left side, a free molecule in solution with energy (E_f) can arrive at wrong position (1) (see Fig. 16) with energy $E(H–H)$ or wrong position (2) with energy $E(T–T)$. To go by way of position (1) to the free state at d and then to correct positions (3) or (4) a greater potential barrier $(\triangle E^*)$ or energy of activation is required than does a molecule going by way of the wrong position (2).

ure 16 with energy E $(T-T)$ on level b of Figure 17, then free itself at d. From d it could migrate to positions (3) or (4) where it would have energy $E(H-T)$ on level c. Thus it goes over an energy barrier $\triangle E^*_2 = E_f - E(T-T)$. Or the molecule could go first to the wrong position (1) of Figure 16, where the binding energy is $E(H-H)$, then free itself and migrate back to positions (3) or (4). The energy barrier (or energy of activation) is $\triangle E^*_1 = E_f - E(H-H)$. The rates of these two processes are $R_2 = KC_f e^{-\triangle E^*_2/KT}$ and $R_1 = KC_f e^{-\triangle E^*_1/KT}$ where K is a constant, C_f is the concentration of free molecules in solution. The ratio of growths in the two directions is $\dfrac{R_1}{R_2} =$

$e^{\dfrac{\triangle E^*_2 \ \triangle E^*_1}{KT}}$ suggesting that in this model, the crystal will grow much faster in the northerly direction.

It has been suggested by M. E. Fleet (priv. comm. 1978) that the water molecules act as an impurity on the negative end of the crystal to account for its slow growth. The fact that uneven growth persists in other solvents such as xylene, *etc.*, directs our attention back to resorcinol molecules wrongly oriented as the possible cause of slow growth on the negative end of the crystal.

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