EXPERIMENTAL TECHNIQUES FOR DETERMINATION OF THE ROLE OF DIFFUSION AND CONVECTION IN CRYSTAL GROWTH FROM SOLUTION

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16. Abstract [as provided in journal]:

"The concentration of the solution around a growing crystal has been studied by many Authors using interferometric techniques.

"A simple description based on the assumption of a purely diffusive mechanism appears inadequate since the convection, effective even in reduced volumes, always affects the growth.

"This has been experimentally shown by holographic interferometric techniques set up in our laboratory."

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EXPERIMENTAL TECHNIQUES FOR DETERMINATION OF THE ROLE OF DIFFUSION AND CONVECTION IN CRYSTAL GROWTH FROM SOLUTION

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The first significant studies of the role of the solution around a growing crystal are probably attributable to Lehmann (1877), who developed various techniques for obtaining a qualitative indication of the concentration field around a crystal. For example, he utilized substances which produced vividly colored colutions, and observed the variations in chromatic intensity near the crystal. /663*

In 1904, Nerst hypothesized that the concentration of the solution in contact with the crystal was the saturation concentration, C_s. But measurement of the index of refraction based on the angle of total internal reflection of $NaClO_3$, $NaNO_3$, $KAl(SO_4)_2$ and $12H_2O$ (as accomplished almost simultaneously by Miers), resulted in a C_0 value for the concentration, such that

$$C_s < C_0 < C_\infty$$

where C_∞ is the concentration of the supersaturated solution far away from the crystal.

Subsequently, Berthoud (1912), Valeton (1924) and Friedel (1926) distinguished two phases in the growth mechanism:

a) material input by diffusion, and
b) incorporation into the crystal,

governed by the following equations: /664

$$dm/dt = (D/d)(C_\infty - C_0) \qquad (1)$$

$$dm/dt = K(C_0 - C_s) \qquad (2)$$

where dm/dt = the quantity of solute at the moment when it is being augmented by diffusion and is being diminished by crystallization;

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*Numbers in the margin indicate pagination in the Italian text.

D = the diffusion coefficient;

d = the width of the layer of solution involved in the diffusion process;

k = the growth rate coefficient of one face of the crystal.

By eliminating C_0, which appears in both equations (1) and (2), we obtain the following equation:

$$dm/dt = \frac{D}{d - (D/K)} (C_\infty - C_s) \qquad (3)$$

where $\frac{D}{d - (D/K)}$ = the effective growth rate coefficient, according to Friedel.

Berg (1938), Bunn (1949) and Humphreys-Owen (1949) measured the concentration by means of an interferometric technique consisting of placing a previously formed $NaClO_3$ crystal in solution between two glass plates which have been silvered so as to be partially reflective, and which form a small angle (see Figure 1). Upon illumination by /665 monochromatic radiation, a system of interference fringes is formed. If the planarity of the plates is accurate, and if the index of refraction of the solution within the angle is uniform, then these fringes are rectilinear.

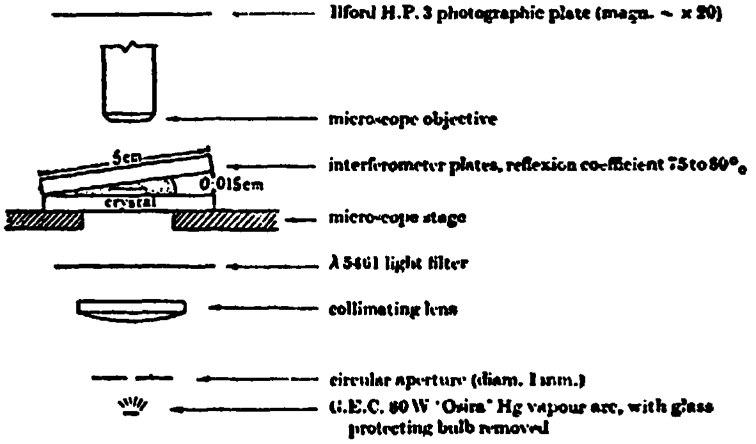

Figure 1. Diagrammatic representation of the apparatus utilized by Humphreys-Owen (Proc.Roy.Soc., 1949, page 220).

Local variations in the index of refraction, due to diminished concentration near the growing crystal, cause the fringes to curve (see Figure 2). This phenomenon makes it possible to evaluate the distribution of the index of refraction, and also the concentration distribution (see Figure 3), based on the linear relationship between these two factors.

Based on the data obtained, it was concluded that the concentration was not uniform along the faces of the crystal but was minimal at the center of the faces, where, on the other hand, the concentration gradient normal to the face was maximal, i.e., proportional to the crystallization flow under the hypothesis that the solute incorporation mechanism is purely diffusive.

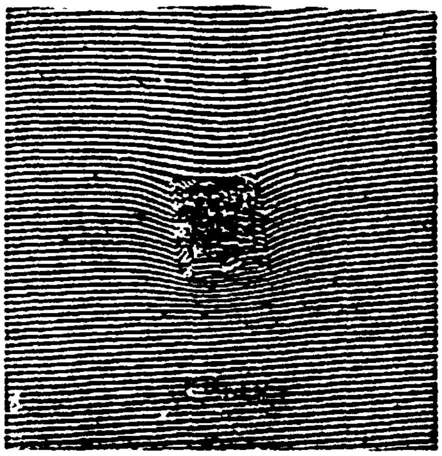

Figure 2. Interference fringes obtained by means of the apparatus shown in Figure 1.

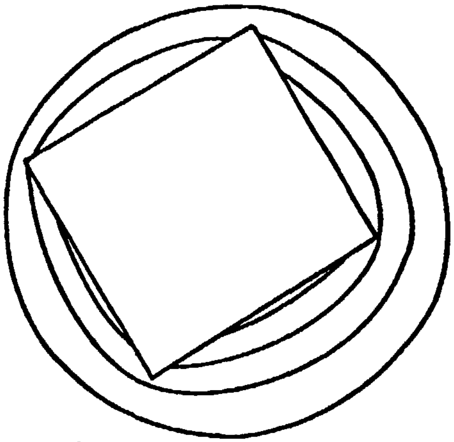

Figure 3. Concentration distribution around a growing crystal, obtained by examination of an interferometric pattern such as that shown in Figure 2.

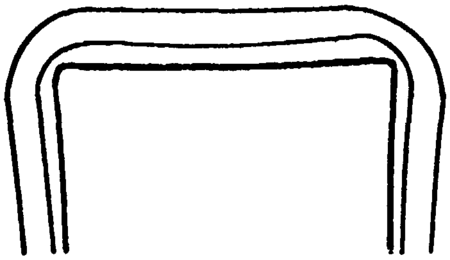

Figure 5. Dendritic growth.

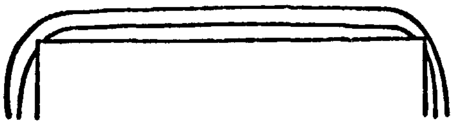

Figure 4. Normal growth.

In order to obtain an immediate qualitative interpretation of the fringes, both Humphreys-Owen and, later, Kreuger and Miller (1953) arranged the semi-silvered plates in a parallel configuration, and obtained the same type of concentration distribution.

However, this method has the disadvantage that the growing crystal does not always completely fill up the space between the two plates. Thus, diffusion occurring relative to the upper face can adversely affect the results.

From the fact that the face grows planimetrically, Berg deduced that there should be a transport of material along the face in one layer, perhaps too slight to be observable by means of the interferometric technique utilized, comprising a transition between the solid and liquid states, similar to that introduced by Vollmer (1932) for melting growth.

During the 1949 Faraday Society conference on crystal growth, /666 Frank opposed this hypothesis on the ground of considerations concerning the average free exchange of solute molecules. He voiced the opinion that, in relation to the geometry of the system, it was not justifiable to leave the convection factor out of consideration. The pressence of convection would of course invalidate the assumption that the solute flow was directly proportional to the normal component of the concentration gradient.

Study of solution growth was advanced by a group of researchers at the University of Strasbourg: Goldsztaub and Kern (1953), Follenius (1959), Quivy (1965), Itti (1966) and Goldsztaub, Itti and Mussard (1969), all of whom utilized polarized white-light interferometric techniques based on a Baker interferential microscope or a dual-refracting Françon interferometer.

In this type of apparatus, two beams interfere so as to create a birefringent beam which passes through the specimen. Thus it is possible to measure the optical delay between the perturbed zone of the solution and a second zone which is far away enough from the crystal to be considered "undisturbed."

Once the specimen is aligned in a parallel configuration, the interference fringes around the crystal are equiconcentrically curved with respect to the solution. Based on the forms of the fringes, it is possible to distinguish two types of growth:

a) regular growth, in which the fringes, which are approximately parallel to the faces, intersect near the corners (Figure 4);
b) dendritic (or skeletal, depending on the nomenclature adopted) growth, in which the fringes follow the contour of the crystal, but without ever intersecting (Figure 5).

The results obtained have been interpreted to a first approximation, taking into consideration diffusion alone, and considering the problem to be two-dimensional. Thus, Fick's equation is utilized:

$$\frac{\partial^2 c}{\partial x^2} - \frac{\partial^2 c}{\partial y^2} = \frac{1}{D} \cdot \frac{\partial c}{\partial t} \qquad (4)$$

In order to integrate Fick's equation (4), the initial condition is posited that at time t = 0, the concentration is constant,

$$c(x,y,0) = C_\infty$$

as are the limit conditions /667

$$c(\infty,t) = C_\infty$$

and the conditions along the face, according to which the growth is classified as either dendritic or regular, respectively:

$$C_0 = \text{constant}, \quad \text{or} \quad \partial c/\partial n = \text{constant}$$

Full integration, as accomplished by Boscher, indicates qualitative agreement between the c(x,y,t) function and experimentally determined fringe development.

The next step consists of comparing the growth rate V_m measured at the center of the face and the growth rate V_c calculated according to the following relation:

$$V_c = \frac{dm}{\rho S dt} = \frac{D}{\rho} \left(\frac{\partial c}{\partial x}\right)_o \qquad (5)$$

where ρ is the density and S is the area.

The solution of the one-dimensional Fick equation,

$$\frac{\partial^2 c}{\partial x^2} = \frac{1}{D} \cdot \frac{\partial c}{\partial t} \qquad (6)$$

with suitable contour conditions, derives from the following relation:

$$c(x,t) = C_0 - (C_\infty - C_0)\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad (7)$$

where

$$\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-u^2}\,du$$

The concentration gradient calculated for x = 0 is:

$$\left(\frac{\partial c}{\partial x}\right)_o = \frac{C_\infty - C_0}{\sqrt{\pi D t}} \qquad (8)$$

Thus, it is possible to calculate V_c and to note that in many instances

$$V_m \simeq 2V_c \qquad (9)$$

The factor of 2 can be explained by the fact that the measured growth rate is an average rate, whereas the calculated growth rate is an instantaneous rate. Consideration of the mean value of V_c during the time interval between T_1 and T_2 yields the following relation:

$$\bar{V}_c = \frac{2}{T_2 - T_1} \cdot \frac{D}{\rho} \left[\left(\frac{\partial c}{\partial x}\right)_{0_1 T_2} T_2 - \left(\frac{\partial c}{\partial x}\right)_{0_1 T_1} T_1 \right] \qquad (10)$$

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Since it has been found experimentally that, except for during the initial period, $(\partial c/\partial x)_o$ remains nearly constant, it can be posited:

$$\left(\frac{\partial c}{\partial x}\right)_{0_1 T_1} \approx \left(\frac{\partial c}{\partial x}\right)_{0_1 T_2} \qquad (11)$$

whereby:

$$V_c = 2\frac{D}{\rho} \left(\frac{\partial c}{\partial x}\right)_o \qquad (12)$$

It must be noted that the apparent relation between V_c and V_m derives solely from application of the relation in equation (11), which cannot be justified on the basis of diffusion alone. Therefore, it is necessary to take into account convection as well.

On the simplified hypothesis that the convection rate is constant with respect to the variation of x and t, the equation governing the transport of material becomes:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + V\frac{\partial c}{\partial x} \qquad (13)$$

where V is the convection rate. For the concentration gradient on the face of the crystal, one obtains the following relation:

$$\left(\frac{\partial c}{\partial x}\right)_o = \left[\frac{C_\infty - C_0}{\sqrt{\pi D t}} - \frac{V}{2D} C_0 \right] e^{-\frac{Vx}{4D}} \qquad (14)$$

By assigning increasing values to the convection rate, the curves illustrated in Figure 6 are obtained. It would appear that the introduction of convection causes a decrease in deviation from the experimental curve.

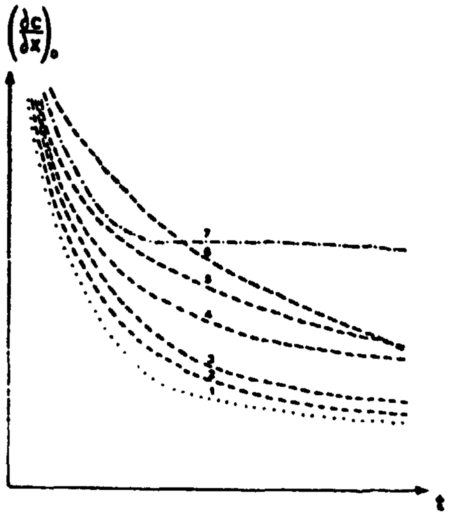

Figure 6. Variation in growth rate as a function of time.

1 = theoretical flow for diffusion alone
2 through 6 = introduction of convection into growth rate calculations
7 = experimental curve

Study of Growth from Solution by Means of Holographic Interferometry

Holographic interferometry (which had previously been utilized in our laboratory in order to obtain a record of the microscopic topography of the surfaces being studied) was applied to the study of growth from solution.

An advantage of holographic interferometry is that it effects a correlation between the two wave fronts and not between the front of the wave being studied and a plane wave, as does conventional interferometry.

Furthermore, the coherence of the laser source utilized makes it possible to study larger volumes of solution, and thus makes it easier to follow the convective phenomena.

An example of the experimental apparatus assembly utilized is shown in Figure 7, and illustrated schematically in Figure 8.

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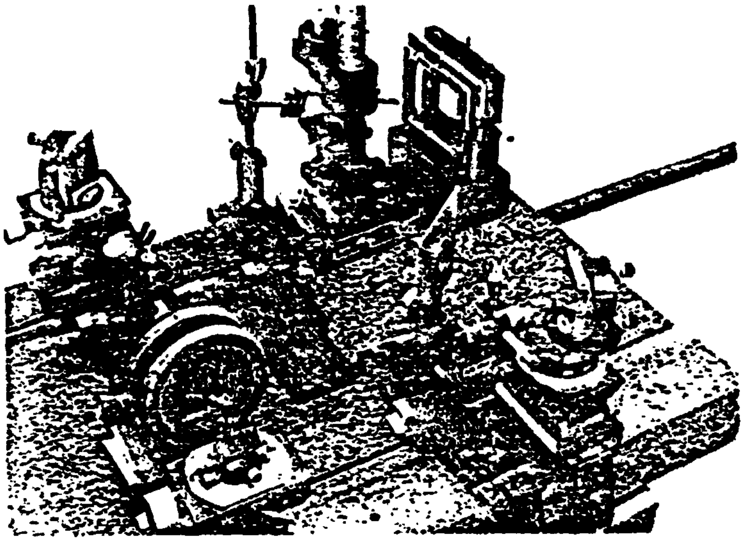

Figure 7. Experimental apparatus assembly utilized to study growth from solution by means of holographic interferometry.

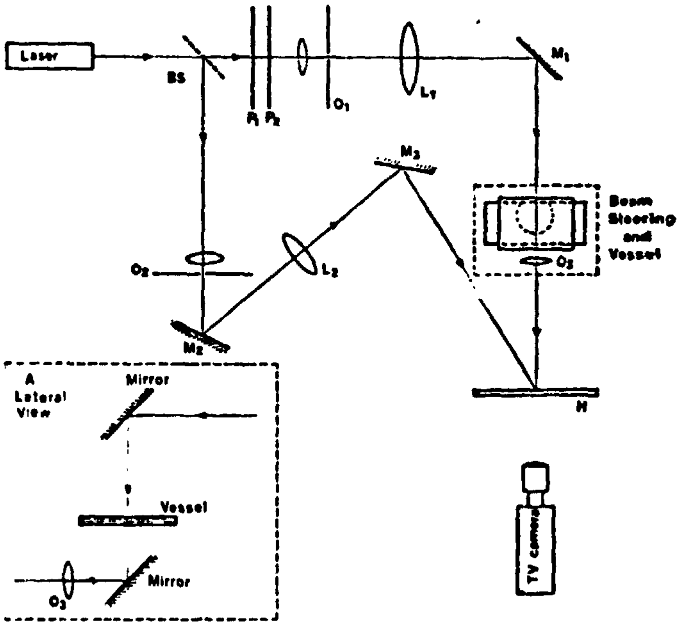

Figure 8. Schematic diagram of the apparatus shown in Figure 7.

BS = beam splitter
P = polarizers
O = objectives
L = lenses
M = mirrors
H = holographic plate

The two collimated laser beams, obtained by means of the beam splitter BS, are enlarged by objectives O and lenses L. One of the two beams passes through the specimen, and the other serves as the reference beam. Both beams are reflected by mirrors M onto the holographic plate H where they interfere, creating a fringe pattern with sinusoidal amplitude transmission and a fringe period on the order of one micron, which can be recorded accurately by the holographic emulsion, due to the latter's high resolution (2500 lines/mm). /670

After development, the plate is replaced exactly in its initial position and illuminated by the reference beam. The microfringe pattern registered on the plate reveals (by means of diffraction) a wave front equal to that which has passed through the specimen.

If there has been any change in the specimen, the wave front which passes through it will be affected, and will interfere with the wave front reconstructed by the hologram, thus creating interference fringes which indicate where an optical change in the specimen has occurred.

This technique, when utilized to follow the evolution of the phenomenon, is termed "real-time" interferometry.

The image of the specimen is filmed by a television camera, recorded by a videorecorder and displayed on a monitor.

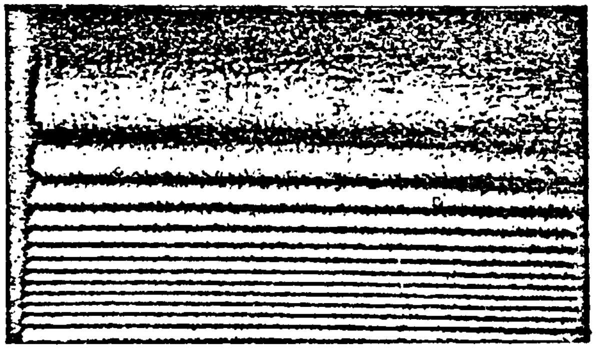

Figure 9. Diffusion fringes in a KCl solution.

The first application of this technique is the determination of the diffusion coefficient for a layer of solution whose concentration is C_0 at a height at which it diffuses toward an overlying solvent column whose height is b - a.

In order to obtain the concentration distribution c(x,t) at level x and time t, it is necessary to solve the Fick equation for the following initial conditions:

$$(x,0) = C_0 \quad \text{for} \quad 0 < x < a$$
$$(x,0) = 0 \quad \text{for} \quad a < x < b$$

which results in a Fourier series of the following type:

$$c(x,t) = C_0 \left[\frac{a}{b} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\sin(\frac{n\pi a}{b}) \cos(\frac{n\pi x}{b})}{n} e^{-\frac{n\pi}{b}^{2} Dt} \right] \qquad (15)$$

The variations in the index of refraction corresponding to changes /671 in concentration are indicated holographically by means of a pattern of horizontal fringes (see Figure 9).

Based on the correspondence between $c(x,t)/C_0$ and the expression /672 $[n(x,t) - n(H_2O)]/n_0$ where n_0 is the index of refraction of the solution having concentration C_0, it is possible to obtain a reasonable value for D of 2×10^{-5} cm^2/sec. for diffusion of a 10% KCl solution.

The growth of $NaClO_3$ in a vessel 20 mm in diameter and 1 mm wide was also studied. The vessel was placed in region "A" of the diagram shown in Figure 8, in horizontal and vertical positions, the better to demonstrate convective movements, with the results shown in Figure 10 and Figure 11, respectively.

Examination of Figure 10 will reveal that the concentration is constant parallel to each face, except near the corners. Simply by counting the number of fringes and referring to the concentration C_∞ of the supersaturated solution at a distance from the crystal, it can be deduc-

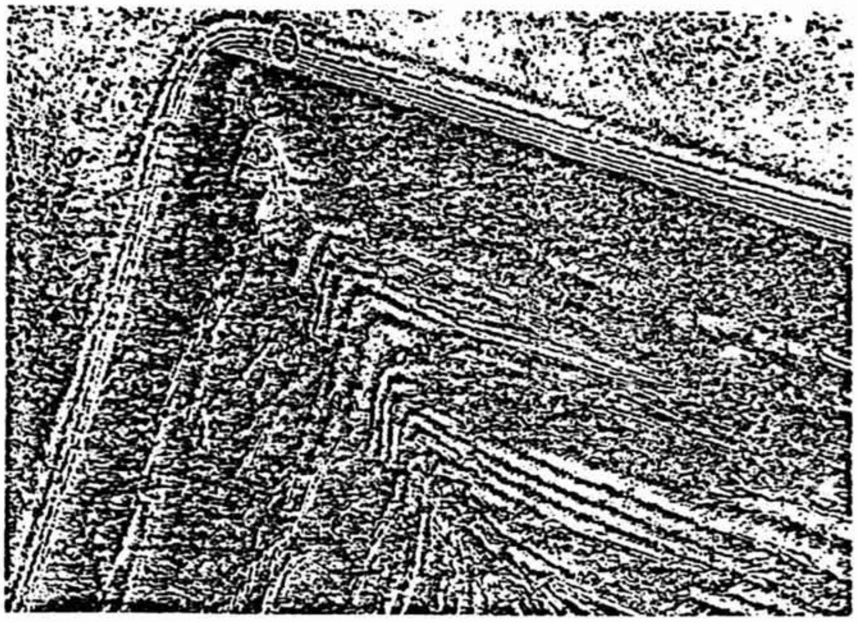

Figure 10. Growth of an $NaClO_3$ crystal: horizontal view of the vessel.

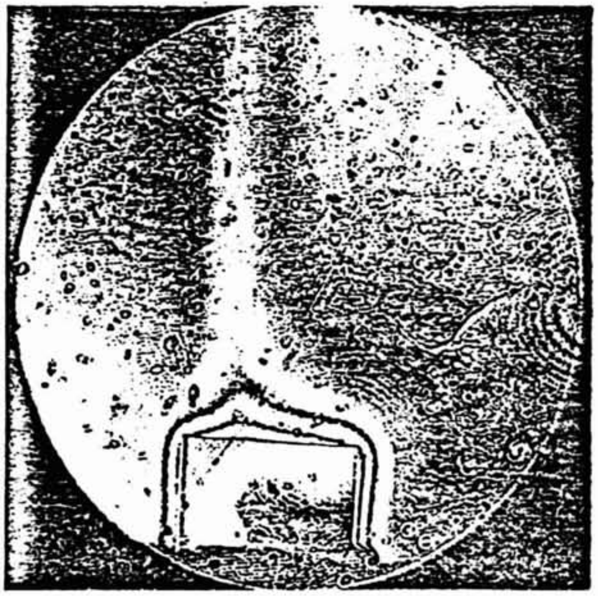

Figure 11. Growth of an $NaClO_3$ crystal: vertical view of the vessel.

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ed that C_0, the concentration of the solution in contact with the crystal, assumes a different value depending on the face being studied, and has a maximum value in relation to the corner.

In Figure 11, it will be noted that, due to the established convective regime, an ascending "chimney" forms in relation to the upper horizontal face of the crystal. This "chimney" allows evacuation of the less supersaturated solution from the zone nearest the crystal. The other, more supersaturated solution replaces it, thus increasing the growth rate.

Tests carried out on solution volumes on the order of 30 cm^3, suitably thermostat-controlled with regard to temperature, have also indicated the predominant role played by convection.

In order to obtain a quantitative interpretation of the experimental results, it will be necessary to work in two different directions:

1) to study capillary growth as Marsiglia B. Simone of the Crystal Growth Mechanism Research Center is doing. If the crystal occupies the entire section of the vertically positioned capillary, then it would appear to be correct to state that the growth of the lower horizontal face is governed by a purely diffusive mechanism. The advantages of the analytic interpretation are opposed by the geometry of the problem, which implies an indirect relationship between the fringes and the concentrations.
2) to replace the television camera with a quadratic photodiode matrix, digitalize the data obtained and analyze them by means of a computer.

It can be hoped that in this way it will be possible to describe the c(x,y,t) function by taking into account both the diffusion and convection mechanisms.

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