

INVESTIGATION OF CONCENTRATION DISTRIBUTION AROUND CRYSTALS IN AQUEOUS SOLUTIONS

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(Presented by Z. Gyulai. — Received 8. I. 1959)

Concentration distribution around growing and dissolving crystals is measured by a phase contrast method. The measurements indicate the existence of a boundary layer around the crystals, as discussed previously by Gyulai.

Introduction

Some years ago GYULAI hit upon the idea that crystals in growth should form a partially ordered boundary layer between themselves and "distant" parts of the solution [1–3].

In the works mentioned above GYULAI presented experimental evidence to prove his statement. Recently, one of us [4] performed direct concentration measurements around growing crystals by a phase contrast method and found some direct evidence for the existence of GYULAI's boundary layer. On the other hand in [4] a second method has been proposed for the investigation of the boundary layer. It was based upon the assumption that the solution of a birefringent crystal (being optically isotropic in its normal state) in the partially ordered boundary layer should possess at least some domains which are optically anisotropic. Such anisotropic domains have been indeed discovered by means of a polarization microscope around growing crystals of some materials (e.g. CuSO_4 , $\text{Na}_2\text{S}_2\text{O}_3$ etc.). Rough estimations of the thickness of the layer were in qualitative agreement with the preliminary results of phase contrast measurements.

The present work aims at a more detailed — and more quantitative — investigation of the boundary layer by the phase contrast method. Our principal interest has been focussed on a possibly unambiguous direct experimental proof of the existence of the boundary layer and on some features of the concentration distribution around a growing crystal. Some other questions (like the dependence of the properties of the boundary layer on circumstances of growth, etc.) are either under investigation or further experiments are planned to study them.

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Experimental procedure

Our measurements have been performed by a Zeiss "general phase contrast device" applied to a Zeiss LGOG type microscope. Aqueous solutions of different materials to be investigated have been put under the objective without any artificial regulation of temperature or evaporation rate, so all our investigations have been performed at room temperature and normal air resp. vapour pressure. Photographs have been taken with a magnification of $150\times$ on a panchromatic film with a sensitivity of 17/10 Din°. They have been evaluated by means of an "Oriphot" densitometer, applied to a microscope with a magnification of $36\times$.

This device enabled us to produce phase contrast pictures of growing, resp. dissolving crystals in a relatively easy manner. It has, however, the disadvantage, that conditions during the process cannot be controlled exactly, so this procedure is not applicable to the investigation of the dependence of the boundary layer on different parameters (temperature, rate of growth etc.).

Durations of expositions have been chosen in such a manner that we worked at the nearly linear part of the characteristic curve of our film. By this means the photometric evaluation of the pictures gave direct information on the relative change of concentration.

Results

Measurements have been performed on the following materials: KBr, $\text{CS}(\text{NH}_2)_2$, $\text{C}_6\text{H}_4(\text{COOH})_2$, $\text{Na}_2\text{S}_2\text{O}_3$.

Results of some typical measurements are plotted in Figs. 1–5. Figs. 1–3

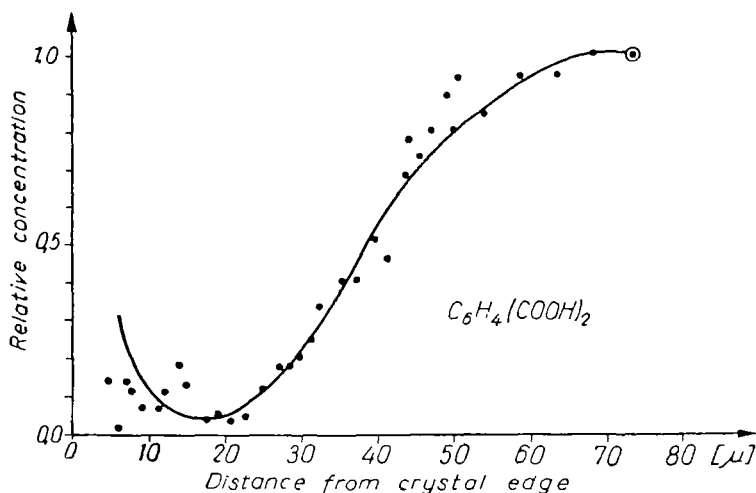


Fig. 1. Relative change of concentration around a $\text{C}_6\text{H}_4(\text{COOH})_2$ crystal in growth. Concentration measured perpendicularly to growing surface, as a function of distance from it. Point of normalization is denoted by a circle (○)

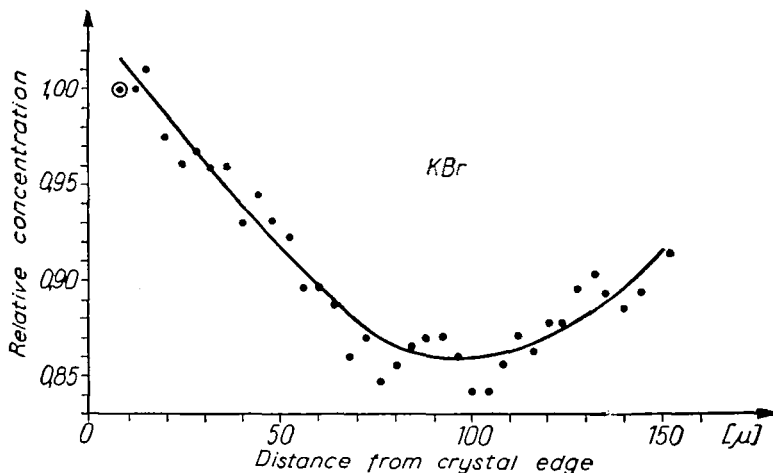


Fig. 2. Relative change of concentration around a KBr crystal perpendicularly to the growing surface, as a function of distance. For the picture of the crystal, see Fig. 6

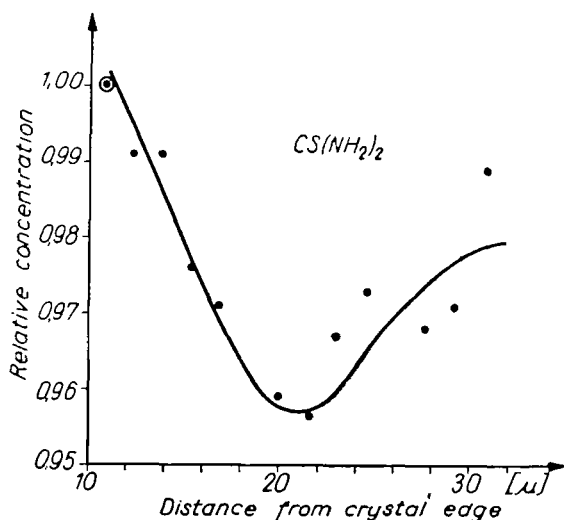


Fig. 3. Relative change of concentration before a CS(NH₂)₂ dendrite growing rapidly

show the relative change of concentration of solution in the neighbourhood of a growing crystal, along a straight line, perpendicular to the growing crystal surface. All the measurements resulted in the characteristic picture of concentration distribution, seen in the first three figures. Approaching the crystal from infinity, concentration first decreases to a minimum, after which it begins to increase monotonously towards the crystal surface. The shape of the curve between its minimum and the crystal surface is — with a rather high accuracy — exponential. Because of the finite width of the photometer slit

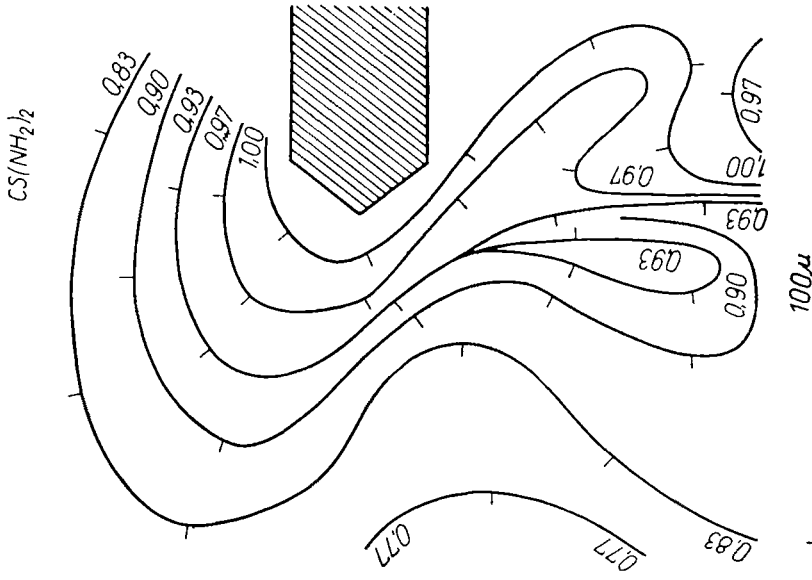


Fig. 5. Distribution of concentration around a growing $\text{CS}(\text{NH}_2)_2$ crystal. Lines of equal concentration are drawn in. The picture of the crystal can be seen in Fig. 9

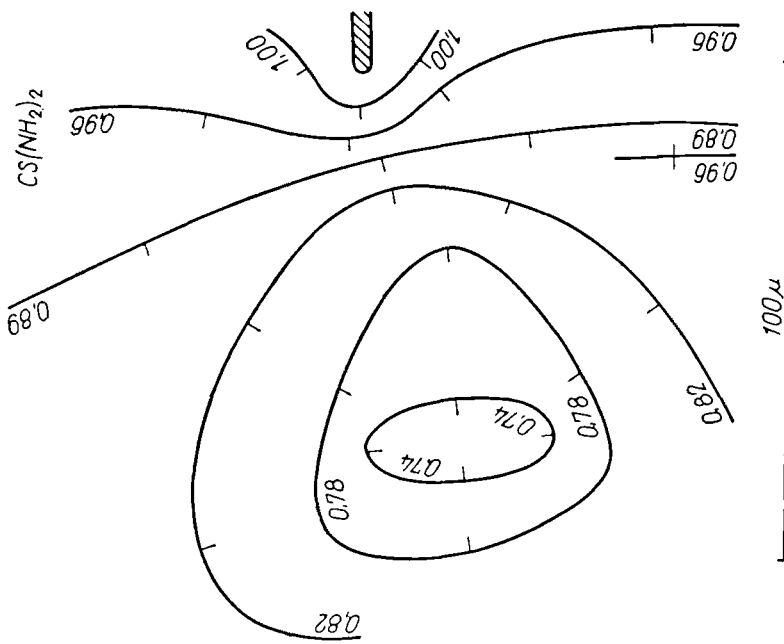


Fig. 4. Distribution of concentration around a $\text{CS}(\text{NH}_2)_2$ dendrite in growth. Lines of equal concentration are drawn in, normalized to that nearest to the crystal. For the photograph of the crystal see Fig. 7

and of diffraction phenomena on the crystal edge, measurements on photographs could be performed only up to a distance of about 10μ from the crystal. If we try to extrapolate the curves to the surface of the crystal, we find that in the immediate neighbourhood of the surface, concentration is 6–25 times as large as at the minimum, and 1,2–3 times as large as the concentration of the solution far from the crystal. The minimum of concentration is generally at a distance of 20–100 μ from the crystal edge. The overall picture of concentration distribution around a growing crystal is to be seen in Fig. 4 and 5.

Lines of equal relative concentrations are drawn in with the indication of the direction of *decrease* of concentration (by a small “thorn” on the isoconcentration lines). One sees that in front of the growing surface isoconcentration lines are densely besides each other, while besides other surfaces the distribution is much flatter. Typical pictures of growing crystals, seen by a phase contrast microscope are presented in Figs. 6–9. Higher concentration (i.e. higher index of refraction) corresponds to a brighter part of the picture. One can clearly recognize the decrease of concentration when approaching the growing part of the crystal, and the domains of higher concentration in the immediate neighbourhood of the growing surface.*

Similar measurements have been performed on crystals in dissolution. The result of a measurement is presented in Fig. 10 (Curve: “experiment”). We plotted in the same figure the concentration distribution which would result from a pure diffusion process and which gives the same concentrations far from the crystal (Curve: “diffusion”).

Discussion and conclusion

Our results seem to contradict theories of crystal growth based on a pure diffusion picture. It has been known for a long time that concentration has a minimum around growing crystals [5] and that matter flows towards this minimum mainly by diffusion. This fact is easy to understand for as matter is built in the growing lattice, the remaining solvent causes a decrease of concentration. What one could not understand in the framework of a pure diffusion picture is, why matter goes forward from the minimum towards the growing lattice, i.e. towards *higher* concentrations. If we take into account the considerations of GYULAI, loc. cit., then this contradiction is automatically resolved. In consequence of the deposition of material on the crystal surface water is continuously set free, which causes the minimum of concentration.

* In order to check our results we performed the same measurements with a small stick of glass immersed in the solution of a material, applied in our measurements. No minimum and re-increase has been found, so we can be almost sure that our results are not caused by optical defects of the apparatus or by the effect of surface tension.

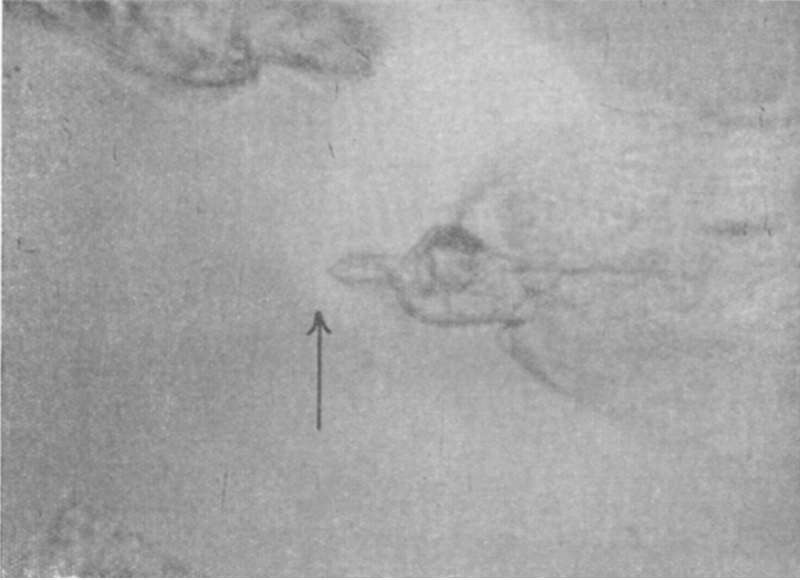


Fig. 7. Photograph of a $\text{CS}(\text{NH}_4)_2$ dendrite in growth (See also Fig. 4)

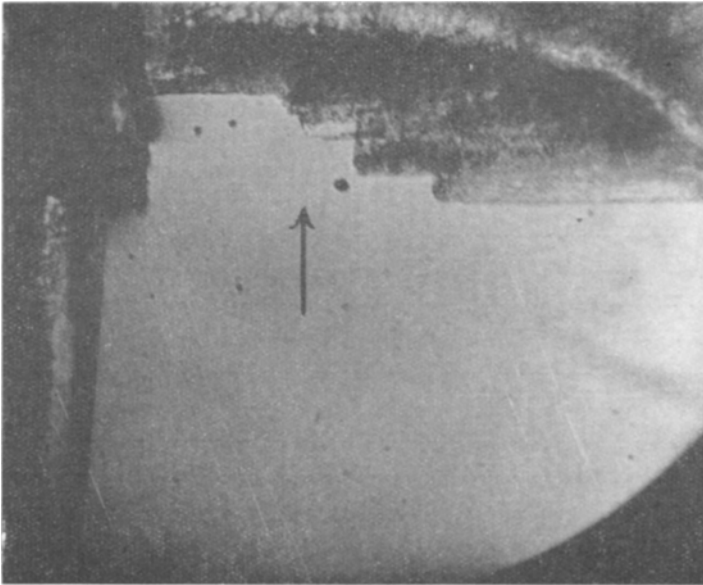
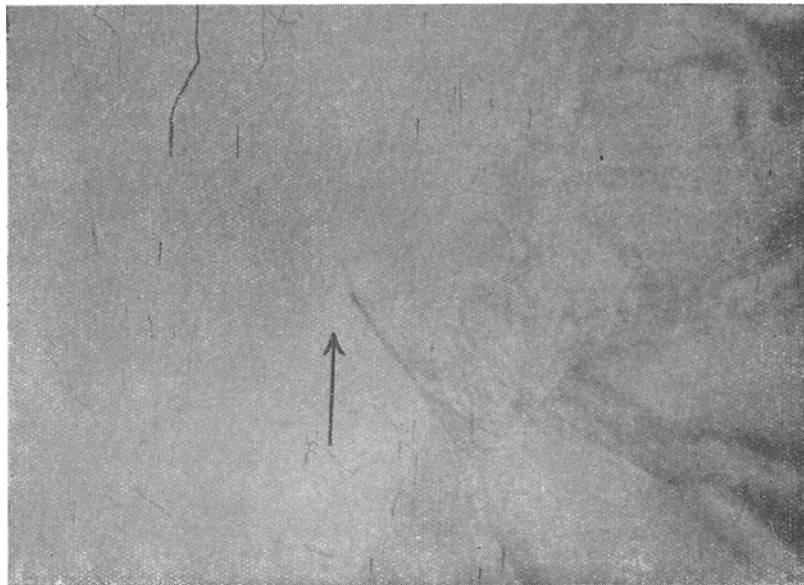
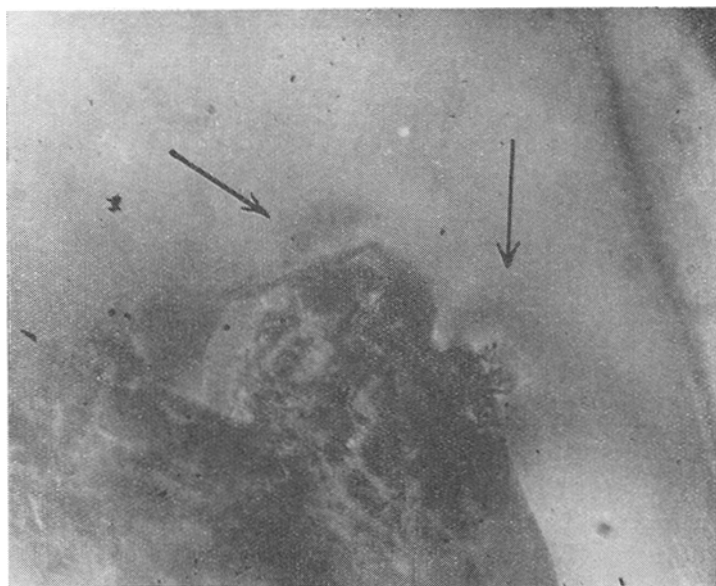


Fig. 6. Lines of growth around the edge of a growing KBr crystal (See Fig. 2)



*Fig. 9. Photograph of a $CS(NH_4)_4$ crystal in growth
(See also Fig. 5)*



*Fig. 8. Photograph of a $C_6H_8(COOH)_4$ crystal in growth.
Note the very strong decrease of concentration (dark)
after a small region of high concentration around the
crystal (bright)*

From the minimum on, towards the crystal surface the increase of concentration and flow of matter are caused by lattice forces, which tend to order material in the lattice structure. The "tail" of the concentration is, however, much longer, than it can be expected from the effect of the lattice only. (In the case of a NaCl-type lattice, these forces are roughly of exponential shape with a range of some times 10^{-8} cm). One can try to explain qualitatively the discrepancy by taking into consideration, that the semi-ordered structure

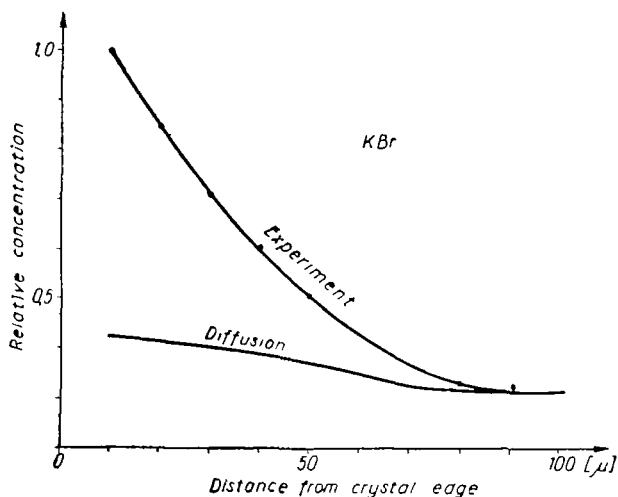


Fig. 10. Change of concentration around a dissolving KBr crystal, as compared with the diffusion theory. Note the significant deviation from theory at distances smaller than $\sim 60 \mu$

around the lattice produces forces of the same character as the lattice itself. So, if there is no violent motion in the solution (not too high temperatures and not very high velocities of growth), one indeed expects a semi-ordered layer to be formed, whose thickness is considerably larger than the range of lattice forces. The average thickness we have found is somewhat larger than GYULAI has estimated, but is of the same order of magnitude. As to the second part of the distribution, namely that from the minimum towards distant parts of the solution, the curve can be represented fairly accurately by an error integral; this latter fact indicates that matter flows from the solution towards the concentration minimum essentially by diffusion.

The existence of a layer of "anomalously" high concentration can be proved in the case of dissolving crystals as well. It is plausible that in a dissolution process the concentration far from the crystal varies according to laws of diffusion. If we fit a concentration distribution, given by the diffusion equation to the experimental distribution at — say — 100μ from the crystal, then we find a significant deviation of the experimental curve at distances smaller than $60-70 \mu$. (Fig. 10.) The strong increase of the

experimental curve compared to the diffusion one, seems to point to the existence of the same semi-ordered layer as observed in the case of growth.

A final result — of course — can be obtained only by observing the *orderedness* of the boundary layer. Our preliminary observations with a polarization microscope seem to be in agreement with those reported here.

Summarizing, we can perhaps conclude that our measurements point to the existence of a boundary layer around crystals in solution. The thickness of it is roughly 50—70 μ , depending on different circumstances, such as temperature, the material considered, etc. This layer is probably to be identified with the boundary layer discussed by GYULAI.

Acknowledgements

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ИССЛЕДОВАНИЕ РАСПРЕДЕЛЕНИЯ КОНЦЕНТРАЦИИ ВОКРУГ КРИСТАЛЛОВ В ОДНОМ РАСТВОРЕ

Г. ДОМОКОШ и Л. МАЛИЧКО

Резюме

Измерено распределение концентрации вокруг растущих и растворяющих кристаллов, с помощью метода фазового контраста. Результаты измерений показывают, что — как это уже показал Дюлаи — вокруг кристаллов имеется переходный слой.