EFFECTS OF GAMMA-IRRADIATION AND ADDITIVES
ON THE GROWTH OF POTASSIUM CHLORIDE CRYSTALS
FROM AQUEOUS SOLUTIONS

by

Gregory D. Botsaris

Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy
at the
Massachusetts Institute of Technology
April, 1965

Signature of Author

Signature of Supervisors

Signature of Head of Department
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EFFECTS OF $\gamma$-IRRADIATION AND ADDITIVES ON THE GROWTH OF POTASSIUM CHLORIDE CRYSTALS FROM AQUEOUS SOLUTIONS

by

Gregory D. Botsaris

Submitted to the Department of Chemical Engineering on April 30, 1965, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering.

ABSTRACT

In this investigation single seed crystals of KCl were grown from aqueous solutions under conditions of constant temperature, supersaturation and impurity concentration. The crystals were held stationary inside the solution while stirring forced the solution to pass the crystal at velocities which depended upon the stirring rate. From the difference in the crystal dimensions before and after growth, growth rates normal to the (100) faces were calculated.

As an outgrowth of this study, the incorporation of Pb$^{++}$ and other ionic impurities in the growing KCl crystals was also investigated.

Four series of experiments were conducted: the first in a solution containing only the impurities inherent in the reagent grade potassium chloride, and the second series in a solution in which small amounts of PbCl$_2$ had been added. The other two series involved the same growth experiments as in the first two; however, they were carried out in a Co$^{60}$ $\gamma$-radiation field (dose rate 2400 rads/min).

Growth Rates of KCl Crystals Grown without Irradiation. The growth rates of the (100) faces of KCl were determined as a function of supersaturation for four concentrations of PbCl$_2$ in the solution: $10^{-8}$ (i.e., "natural" lead content), $10^{-7}$, $10^{-6}$ and $10^{-5}$ moles per mole KCl. Cabrera-Vermilyea and Frank's mechanism was used to explain qualitatively the observed dependence.
The conditions under which the growth rate is not controlled by diffusional processes (of the principal solute or of the lead ions) in the liquid were determined experimentally. The data were successfully correlated with the Froessling equation.

The role of impurity diffusion in the crystallization process in general was emphasized.

Growth of KCl Crystals in a $\gamma$-radiation Field. The observed effects of the radiation were:

a) at certain levels of lead concentration, irradiation decreased the growth rate of the (100) faces relative to the rate at the same impurity level. A mechanism is suggested involving enhancement of the diffusion of lead in the crystal by the $\gamma$-rays.

b) irradiation reduced the dislocation density of crystals grown from solutions containing no added PbCl$_2$ relative to crystals grown from the same mother solution, but without irradiation.

Incorporation of Impurities during KCl Crystal Growth (without Irradiation). Using emission spectrography as a method of analysis, the distribution of various metal-ion impurities between the grown KCl crystal and the solution was studied. The distribution coefficients, defined as ratio of the impurity concentration in the crystal to the concentration in solution for certain ions (Pb$^{++}$ and Fe$^{+++}$), were found to be greater than unity at very low concentrations. The lead distribution coefficients ranged from 2700 (for solutions containing $10^{-8}$ moles Pb/mole KCl) to 28 (for solutions of $10^{-5}$ moles Pb/mole KCl).

The results on hand suggested a mechanism of non-equilibrium capture of the impurity according to which the magnitude of the distribution coefficient in such cases depends on the equilibrium distribution coefficient between the solution and surface of the crystal, the rate of growth of the crystal, and the rate of diffusion of the impurity through the crystal lattice.

These findings are believed to be of significance in the purification of materials by fractional crystallization. For instance, they indicate that in order to produce crystals of KCl free from Pb$^{++}$ and Fe$^{+++}$, the conventional techniques of recrystallization should be modified to include rejection of the first crystals grown.

Thesis Supervisors: E. A. Mason, Professor of Nuclear Engineering
R. C. Reid, Professor of Chemical Engineering
April 30, 1965

Professor Philip Franklin
Secretary of the Faculty
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Cambridge, Massachusetts 02139

Dear Sir:

The thesis entitled "Effects of γ-irradiation and Additives on the Growth of Potassium Chloride Crystals from Aqueous Solutions" is herewith submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Respectfully submitted,

Signature redacted

Gregory D. Botsaris
The conditions under which the growth rate is not controlled by diffusional processes (of the principal point to in the legions) in the liquid were determined experimentally. The data were successfully correlated with the following equation.

Department of Chemical Engineering
M. S. thesis, University of California, Berkeley

Grown on 111 surfaces of LiF substrates. The observations on the radiation were:

1. At certain levels of lead concentration, irradiation depressed the growth rate of the (111) faces relative to the rate of the same dopant levels in the regions involving enhanced growth in the crystal by the action of the microscopically fast of the external factors.

2. Irradiation reduced the growth rate of the (111) faces relative to the rate at the same dopant levels, suggesting involved enhanced growth in the crystal by the microscopically fast of the external factors.

The results of our study, together with the data presented in this section, indicate that the pure growth rate of LiF single crystals under the conditions of the experiment is controlled by the diffusion of the impurities through the crystal lattice.

From these findings, it appears likely that in the purification of materials by fractional crystallization, for instance, may indicate that in order to produce crystals of high purity from the molten LiF, the conventional techniques of purification should be modified to include rapid quenching of the melt crystals grown.

M. S. thesis, University of California, Berkeley

W. J. Hill, Professor of Chemical Engineering

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To my uncle Harry Chilliras
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CHAPTER I
SUMMARY

1. SCOPE

The object of this study was the determination of the effect of gamma radiation on the rate of growth of seed potassium chloride crystals from supersaturated solutions. As an outgrowth of this study, the effect of Pb++ and other heavy metal ions on (a) the growth rate and (b) crystal purity of potassium chloride was also investigated.

The gamma-irradiation studies were initiated since it is known that radiation of crystals can produce lattice defects of various types, and it was hypothesized that creation of such defects could alter noticeably the crystal growth rates.

The impurity (primarily Pb++) studies resulted from the ad hoc finding that growth rate-retardation ions must be added to a saturated potassium chloride solution to provide a supersaturation ratio large enough to measure conveniently, without simultaneously triggering spontaneous nucleation. Spontaneous nucleation was especially favored in the supersaturated solutions exposed to a radiation environment. Lead was chosen because it is known to be very effective in suppressing nucleation in KCl solutions (18).
2. CONCLUSIONS

The principal conclusions reached during this study can be summarized as follows.

a) Growth of KCl crystals without irradiation

i) Lead chloride decreased the growth rate of the (100) faces of KCl even in solutions containing as low as $10^{-8}$ moles PbCl$_2$/mole KCl. The decrease became more important as the PbCl$_2$ concentration increased and the supersaturation level decreased.

ii) Reagent grade KCl, used for the preparation of the supersaturated solutions, was found to contain lead at the level of $10^{-8}$ moles/mole KCl. Thus, growth rates from a truly pure solution have not been obtained.

iii) Growth rates (with or without added lead) of KCl crystals increased rapidly with supersaturation level. The change to rapid dendritic growth occurred within a very small supersaturation range, for instance from 0.17 to 0.20% supersaturation for a solution containing no added PbCl$_2$. The drastic increase is consistent with Cabrera-Frank's model of time-dependent adsorption of impurities on a crystal surface.

iv) Crystal growth rates were not mass transfer controlled except at high supersaturations when dendritic growth occurred, or when low stirring rates were employed. At low stirring rates either the mass transfer of the
principal solute (KCl) became controlling (in solutions without added lead) or the mass transfer of the impurity lead (in solutions with added lead). In the former case the growth rate decreased, and in the latter, increased as the stirring rate decreased.

v) Secondary nucleation always accompanied the formation of dendrites. The idea that secondary nuclei originate from broken dendritic branches is thus supported.

b) Growth of KCl crystals in a γ-radiation field

i) Effect of γ-irradiation on dislocation density

Potassium chloride crystals grown under Co\textsuperscript{60} γ-irradiation (dose rate 2400 rad/min) from solutions containing no added PbCl\textsubscript{2} showed a slightly reduced dislocation density relative to crystals grown from the same mother solution, but without irradiation.

It is suggested that a dislocation climb process is responsible for the observed reduction.

Irradiation had no effect on the dislocation density of crystals grown from solutions containing 10\textsuperscript{-7} moles PbCl\textsubscript{2}/mole KCl.

ii) Effect of γ-irradiation on the growth rate

Irradiation of 2400 rad/min dose rate had no effect on the growth rate of the (100) faces of KCl crystals grown from solutions containing no added PbCl\textsubscript{2} and solutions containing 10\textsuperscript{-6} moles PbCl\textsubscript{2}/mole KCl.
However it decreased the growth rate of the (100) faces relative to the rate at the same impurity level, when the lead concentration in the solution was $10^{-7}$ moles/mole KCl.

c) Incorporation of impurities during KCl crystal growth (without irradiation)

i) Potassium chloride crystals grown from solutions containing lead ions in concentrations less than $10^{-5}$ moles Pb/mole KCl will contain a higher concentration of lead than in the crystallizing solution.

ii) Lead distribution coefficients, crystal-to-solution, ranged from 2700 to 28. The coefficients decreased as the lead concentration was increased.

iii) For a given constant lead concentration in the solution (i.e., $10^{-7}$ moles/mole KCl) the lead concentration in the KCl crystals decreased as the growth rate increased.

iv) The incorporation of Fe$^{+++}$, Ti$^{+++}$, Bi$^{+++}$, Hg$^{++}$ by the growing KCl crystals was also tested. For certain solution concentrations, iron and titanium presented effective distribution coefficients larger than unity; bismuth and mercury did not under any of the concentrations used.

v) The results indicate that in order to produce ultrapure crystals of KCl (free from Pb$^{++}$ and Fe$^{+++}$),
the conventional techniques of recrystallization should be modified to include rejection of the first crystals grown.

3. EXPERIMENTAL PROCEDURE

   a) Growth experiments without irradiation

   Single seed crystals of potassium chloride were grown under conditions of constant temperature, supersaturation and impurity concentration. These seeds were cleaved from larger melt crystals. As used the seeds were rectangular parallelepipseds with only \((100)\) faces. Their dimensions were from 1 to 2 mm.

   Growth studies were carried out in a crystallizer flask containing a supersaturated solution of potassium chloride. Seeds were held in place by tweezers. Growth could then occur naturally on only four of the six possible faces. The solution was stirred vigorously. Growth rates were not mass transfer controlled as the stirring rate was always maintained sufficiently high that variations in the rate produced no noticeable effect on the growth rates.

   Evaporation of the solution during the studies was prevented by seals in the crystallizer flask. The temperature was held constant to \(\pm 0.01^\circ\text{C}\). A schematic drawing of the experimental equipment is shown in Figure 1.

   The depletion of the solution by the growing crystal,
with respect to both solute and additives, was negligible.

The saturated solutions were prepared by mixing an excess of reagent grade KCl ("Baker Analyzed") with triple distilled water and stirring the mixture for at least 18 hours. During this time the flask was held in a constant temperature bath at + 0.01°C (Figure 1). The saturated solution was transferred to the crystallizer flask through a heated glass tubing. In this transfer a sintered glass filter in the glass tube prevented carry-over of undissolved crystals.

The supersaturation was determined from the difference of the temperatures in the saturation and the crystallization flasks. The saturation temperature was usually adjusted so that the desired supersaturation would be obtained at a constant growth temperature of 35°C.

Supersaturation was defined as the ratio $\frac{C_L - C^0}{C^0}$ where

$C_L$ = the actual solution concentration

and

$C^0_L$ = the solubility at the crystallization temperature.

This ratio multiplied by one hundred expresses the percent supersaturation.

The dimensions of the crystal were measured under a microscope (50X magnification) before and after growth.
From the difference of the two measurements over the duration of growth (1 to 8 hours), the growth rates normal to each face were calculated.

b) Growth experiments under irradiation

Radiation of growing potassium chloride crystals was carried out in the Co$^{60}$ source operated by the Department of Nutrition and Food Science of M.I.T.

This source consists of Co$^{60}$ pellets (total intensity 32 Kilocurie) sealed inside cylinders and located at the bottom of a water-filled tank 12 feet deep. Crystallization experiments were carried out in a water-tight box which was held at a height chosen to give the desired radiation flux (maximum radiation dose rate 2400 rad/min). Inside the water-tight box were the crystallizer flask, constant temperature bath, stirrers, etc. A cable connected to the box allowed power feed and temperature measurements to be made during the run. A schematic drawing is shown in Figure 2.

E) Determination of the impurity content of the KCl crystals

Impurity concentrations in the dry KCl crystals were determined spectrographically by Farrell-Ash Company (Waltham, Mass.). The lower impurity levels which could be detected by the method were: 0.1 ppm for Pb and Fe, 0.5 ppm for Bi, 1 ppm for Ti, and 10 ppm for Hg.
4. DISCUSSION-GROWTH OF KCl CRYSTALS WITHOUT IRRADIATION

a) Previous work

There have been only a few studies yet reported in the literature where the emphasis has been on the effect of impurity level on the absolute growth rate of the crystal faces. In the particular case of KCl, it has been reported (180,102) that lead ion impurities caused the appearance of (110) and (111) faces presumably by reducing the relative growth rates of these faces compared to the (100) face.

Sears (153), however, observed qualitatively a reduction of the growth rate of the (100) face by 1 ppm PbCl₂ in the solution. It appears, then, that lead will reduce the growth rates of all the above-mentioned faces of the KCl crystal.

In this investigation a quantitative study of the effect of PbCl₂ on the growth rate of a (100) face of KCl was undertaken; the variables studied were the supersaturation, the concentration of the PbCl₂ in the solution and the stirring rate in the crystallizer.

b) Growth rates of (100) faces as a function of the supersaturation and the lead concentration

During this investigation it did not become possible to grow KCl crystals from a truly pure solution and use such data as a reference. Crystal growth rate measurements
indicated that even "pure" solutions, prepared from reagent grade KCl contained lead in the order of $10^{-8}$ moles/mole KCl. In addition, the exact concentration of lead varied from bottle to bottle of the reagent. This variation was sufficient to cause variation in the growth rate data obtained from different "mother" solutions.

Thus, the value of $10^{-8}$ moles Pb/mole KCl constituted the lowest lead concentration studied; the highest value was $1 \times 10^{-5}$ moles Pb/mole KCl.

The experimental growth rate data have been plotted in Figure 3. Values higher than 160 $\mu$/hr indicate dendritic (non-layer) growth. Measurement usually was not possible, because the dendritic crystal did not present a definite edge. It was concluded, however, that the growth rate was higher than 160 $\mu$/hr.

The growth rate measurements obtained from different "mother" solutions, which contained the same concentration of added PbCl$_2$, did not always fit the same curve in the diagram of Figure 3. For instance, the data from one of the solutions containing $10^{-7}$ moles added PbCl$_2$/mole KCl fitted curve B', while the data from two other solutions of the same lead concentration fitted curve B. Also, one of the solutions containing $10^{-6}$ moles fitted curve C', while four others fitted curve C. The variation appears to damp out when using solutions containing $10^{-5}$ moles PbCl$_2$/mole KCl.
This lack of reproducibility has been attributed to variations in the purity of the growth solutions. The fluctuations in the impurity content of the reagent KCl is one of the factors responsible; others might also contribute.

(1) Variation in impurity content due to the saturation procedure. Depending on the procedure followed for saturation, the amount of lead precipitated, and thereby the amount remained in solution, will vary. (See discussion in Section 6.)

(2) Introduction of impurities by the metallic parts of the crystallizer. Higher growth rates were obtained in an all-glass crystallizer than in one containing stainless steel parts (shaft and crystal holders).

(3) Variation in the amount of added PbCl₂. One drop of a concentrated solution of PbCl₂ was usually added in the crystallizer. The volume of the drop could fluctuate.

The growth rate data indicate that the effects of lead chloride are strongly dependent on the supersaturation and the lead concentration in the solution. A drastic increase in the growth rate (for a given concentration of lead) is observed when a certain supersaturation level is attained.

To explain the above dependence, the mechanism by which lead affects the growth on the (100) faces should be considered.
c) Mechanism by which lead retards growth on the (100) faces

It is generally believed that to be effective in altering the growth on a crystal face, an impurity must adsorb to a certain extent on that particular face. According to Sears (152,154), the impurity is adsorbed on the growth steps poisoning the active growth sites, i.e., the kinks, and is not necessarily incorporated into the crystal.

Cabrera and Vermilyea (47), however, suggested that the adsorption of the impurity takes place on the plane regions between steps. The velocity of the growth steps is reduced, since they are forced to pass through the adsorbed impurity atoms. Obviously only immobile impurities, strongly adsorbed, are effective in this mechanism. The adsorbed impurities in this case are buried inside the growing crystal. The same mechanism was also proposed by Frank (73). In addition, he emphasized the notion that the concentration of the impurities on the crystal surface is time dependent.

Booth (12) has found by the use of autoradiographs that in NaCl, Pb is incorporated along the (100), but not the (111) faces. It could be assumed that the behavior of Pb in KCl is the same, since the effect of lead on the habit of KCl and NaCl is the same in both salts (180). Thus, Sear's mechanism is more probable to act on (111) faces. Since the ionic arrangement on a (111) face and
in a kink on a growing (100) face are the same, Sear's mechanism may act on the (100) also. However, since incorporation does take place on the (100) planes, an additional mechanism should be operating. This could be the mechanism suggested by Cabrera-Vermilyea and Frank; in other words, on the (100) faces lead is adsorbed, not only at the kink sites of the advancing steps, but also on the surface.

The Cabrera-Frank model can offer a qualitative explanation for the drastic increase in growth rate when a certain supersaturation level is attained: when the supersaturation increases, the step flux increases; the spacing between steps thereby becomes smaller. For a given step velocity, therefore, less time is allowed for lead ions to adsorb before the next step passes. The steps would begin to encounter smaller impurity concentrations on the surface, and their rate would increase. This rate increase, however, would allow less time for the lead ions to adsorb, and their concentration on the planar regions between steps would be further reduced. A cascading effect is developed in this way that can account for the abrupt change in the growth rate for small changes in supersaturation.

A similar cascading effect is expected with increasing lead concentration (for a given supersaturation). It can explain the drastically increased effectiveness of lead at high concentrations.
d) Effect of stirring rate on growth rate from solutions containing no added PbCl₂ - Region where mass transfer is the controlling rate.

The effect of stirring rate on the growth rate was studied by growing crystals at different stirring rates and in the same solution. The results for two solutions are presented in Figure 4 as Curves A and B. The supersaturation is the same for both solutions. The difference in growth rates is presumably due to the difference in impurity content.

Inspection of Figure 4 shows that at low growth rates the growth rate was independent of the stirring rate (or the liquid velocity) for stirring rates ranging from 600 to 1200 rpm. At high growth rates, however, the growth rate increased as the stirring rate increased from 400 to 850 rpm and then became independent of the liquid velocity.

It is concluded, therefore, that for 0.12% supersaturation when a stirring rate in the crystallizer higher than 850 rpm was employed, the liquid mass transport was not the controlling resistance, as long as the crystals were growing at a rate less than about 150 μ/hr. For lower growth rates the minimum stirring rate could be less than 850 rpm. In all the growth experiments performed in this investigation, at 0.12% supersaturation, stirring rates higher than 850 rpm were employed.
e) Theoretical correlations - Froessling equation

The semi-empirical equation developed by Froessling (75)

\[ N_{Sh} = 2 + 0.552(N_{Re,S})^{2}(N_{Sc})^{3} \]  

where

- \( N_{Sh} \) = Sherwood number, \( K_d/D_v \)
- \( N_{Re,S} \) = sphere Reynolds number, \( \frac{dU_p}{\mu} \)
- \( N_{Sc} \) = Schmidt number, \( \frac{\mu}{\rho D_v} \)
- \( K \) = mass transfer coefficient, cm/sec
- \( D_v \) = diffusion coefficient, cm\(^2\)/sec
- \( d \) = sphere diameter, cm
- \( \rho \) = solution density, gm/cm\(^3\)
- \( U \) = liquid velocity, cm/sec
- \( \mu \) = solution viscosity, gm/cm/sec

was used to calculate the mass transfer coefficient for crystals of KCl growing at 0.12% supersaturation and 35\(^\circ\)C temperature. (The liquid velocities corresponding to 650, 900 and 1100 rpm were found to correspond to liquid velocities of 43, 49 and 61 cm/sec.) From them mass transfer rates were calculated, which are plotted in Figure 4 as curve C.

The calculated curve is remarkably close to the part of the experimental curve where the mass transfer is
presumably the controlling rate.

f) Dendritic Growth and secondary nucleation

Figure 4 indicates that for stirring rates around 1000 rpm, the liquid phase mass transport resistance becomes important when the growth rate exceeds the value of 160 μ/hr. Two phenomena were observed in this investigation in association with growth rates higher than 160 μ/hr: dendritic growth and secondary nucleation. The explanation is that dendritic formation is favored when the mass transfer resistance is controlling, while the secondary nuclei originate from broken dendritic branches.

It should be noted that primary nucleation in the KCl solutions was observed only in supersaturations higher than 0.35%.

g) Effect of stirring rate on growth rate from solutions with added PbCl₂ (10⁻⁷ moles/mole KCl)

Growth rate curves as a function of stirring for two different solutions are presented in Figure 5. A third solution gave a curve similar to A. Pictures of four crystals from the solution of curve A (each one for a different stirring rate) are presented in Figure 6.

It is observed from Figure 5 that at low growth rates (curve B) the growth rate was independent of the stirrer speed, at least for the range of 400 to 1100 rpm. At higher growth rates, however (curve A), when the
stirring rate was reduced below 1000 rpm, the growth rate increased rapidly.

As the photographs in Figure 6 show, this increased growth is not a planar growth. Actually it results from clusters of small crystallites which appear on the crystal surface at low stirring rates. In some cases (as in crystal 5 - Figures 5 and 6), the clusters did not cover the whole surface; the basic planes of the cubic seed could be observed and their advancement be measured. This is the reason two growth rates (5 and 5* in curve A) are reported for the same crystal.

Although the growth at low stirring rates is not a layer growth, it is indeed an increased growth, especially if expressed in mass units. This increased growth rate can be explained by assuming that at low stirring rates the mass transfer of the lead ions through the liquid phase becomes important. Roughly speaking, as the liquid velocity decreases, the amount of lead which diffuses to the crystal is reduced, and the retardation of the KCl growth becomes smaller.

It is believed that the role of the impurity diffusion through the liquid has not been adequately recognized in the crystallization process, in contrast to the recognition given to the role of the solute diffusion. It is suspected, for instance, that the crystallization experiments in the presence of additives, which have been reported
in the literature and in which slow or no stirring was provided, the diffusion of the impurity was probably the controlling rate. That means that the effect of those impurities on the crystal habit or the growth rate was grossly underestimated.

**h) Mechanism of formation of the crystal clusters**

The following mechanism is suggested: It will be shown in Section 6 that a large amount of lead is adsorbed and subsequently incorporated into the growing crystal of KCl. At low stirring rates this will result in very low lead concentrations in the region of the liquid close to the crystal surface (inside the boundary layer).

The supersaturation, however, in that region can be high enough (a calculation showed at least 0.36% supersaturation) to initiate formation of new crystal nuclei in the absence of lead. Some of these nuclei could drift towards the solution and grow to independent crystals (secondary nucleation), while others will remain inside the layer and start growing more rapidly, especially in the direction of the least lead concentration, i.e., towards the crystal surface. There they will join the growing face. The nuclei, however, by growing will deplete the solution around them further and will initiate new nucleation. This kind of chain nucleation could lead to the observed cluster formations at low stirring rates.
5. DISCUSSION-GROWTH OF KC1 CRYSTALS IN A γ-RADIATION FIELD

Irradiation of growing crystals should affect the crystal structure. These changes in the crystal lattice may in turn affect the growth rate of the crystal. Both these effects were studied a) by determining the dislocation densities, and b) measuring the growth rates of the crystals grown in a γ-radiation field. These were then compared to similar measurements from crystals grown without irradiation.

a) Effect of γ-irradiation on the dislocation density of KC1 crystals

Etching Procedure. The etching technique used was similar to that suggested by Anokhina et al. In brief, the crystals were etched by immersing them into anhydrous methanol (saturated with ammonium chloride) for thirty seconds. The temperature of the methanol solution was adjusted to be between 26 and 30°C. The crystals were rinsed by dipping them into anhydrous n-butyl alcohol.

This solution gives reproducible etch pit patterns; the mirror image correspondence between the two cleaved surfaces of a crystal was satisfactory. (See Figure 7.) Each cleaved surface consisted of two parts: that belonging to the original seed crystal and the grown part, which enclosed the former.

The density of the pits was determined over those
small areas of the crystal belonging to the grown part, as well as in adjacent points belonging to the seed. The pits were counted under a microscope (1000X magnification) by the use of a ruled grid in the eyepiece.

**Results from Dislocation Density Measurements.** The dislocation densities were determined in crystals taken from the following four groups:

1. No PbCl$_2$ added in the solution - no irradiation.
2. No PbCl$_2$ added in the solution - irradiation (2400 rad/min).
3. $10^{-7}$ moles PbCl$_2$/mole KCl added - no irradiation.
4. $10^{-7}$ moles PbCl$_2$/mole KCl added - irradiation (2400 rad/min).

The results are presented in Figure 8; the dislocation density of the grown part is plotted as the ordinate, while the corresponding dislocation density of the adjacent seed crystal part as the abscissa.

It is concluded from the data that in general the dislocation densities of the crystals grown from solution do not differ greatly from the seed crystals, which had been obtained from melt. In two of the above cases, however, - namely (3) and (4) - a slight increase in dislocation density was noted, while in case (2) irradiation generally resulted in a small decrease.

More specifically, the KCl crystals grown under $\gamma$-irradiation without PbCl$_2$ addition contained in the
major portion of their volume from 0.5 to $1.1 \times 10^7$ dislocations/cm$^2$. However KCl crystals grown without irradiation, as well as crystals grown under irradiation but after PbCl$_2$ addition, in no case contained less than $1.4 \times 10^7$ dislocations/cm$^2$.

Figure 9 shows the etch pit pattern in a grown crystal in which the dislocation density has been reduced by the $\gamma$-irradiation. (Picture 11. See also Figure 10.) The other three pictures in Figure 9 represent the cases where no reduction in the dislocation density occurred.

**Mechanism for the Reduction in Dislocation Density by $\gamma$-Irradiation.** It is suggested that a dislocation climb process is responsible for the observed lower dislocation density in crystals grown in a radiation field. The same number of dislocations are formed under irradiation, but a fraction of them "climb out" during the growth.

The dislocation planes in a KCl crystal contain both positive potassium ions and negative chlorine ions (22). Thus, for a dislocation to climb, both positive ion and negative ion vacancies should be absorbed by the dislocation plane. The negative ion vacancies can be produced in the crystal by the $\gamma$-rays (probably by a Varley mechanism). The positive ion vacancies exist in the crystal lattice to compensate for the charge of the multivalent impurities (for instance, Pb$^{++}$ and Fe$^{+++}$).

Calculations indicate that there were $2.7 \times 10^9$
vacancies available in the crystal for each one of those dislocations which disappeared. This number indicates that the dislocation climb is not impossible, especially when one considers that a dislocation in a growing crystal could interact with these vacancies, while it is still close to the surface and the length of the extra plane is comparatively small.

A speculative explanation for the experimental fact that γ-irradiation fails to reduce the dislocation density in crystals grown from solutions of $10^{-7}$ moles Pb/mole KCl concentration is offered: lead, under the ion or metal form, is collected at the dislocations, making their climb more difficult. That impurities can impede the climb of dislocations was assumed first by Boas \(17\). Mott \(129\) has suggested that this is due probably to the adsorption of impurity atoms at the dislocation jogs; jogs are the points where vacancies would "condense". The lead would, thus, prevent the vacancy "condensation" and slow down the climb process.

b) Effect of γ-irradiation on the growth rate of (100) faces of KCl crystals

It was pointed out in Section 4 that different solutions manifest different growth rates under identical conditions. This was attributed to fluctuations in the impurity content among the solutions.

For this reason experiments were designed in such a
way that for each growth rate measurement under irradiation, a growth rate measurement was taken from the same solution and under the same conditions (supersaturation and stirring rate) but outside the radiation field; i.e., the container was placed at the top of the tank (Figure 2) where the radiation dose rate is practically zero. The following method of plotting growth rate results was chosen: the growth rate under irradiation is plotted against the growth rate without irradiation from the same solution; if the line passing through these points coincides with the 45° line, the irradiation is assumed not to affect the growth rate, while if the line lies below it, irradiation retards growth.

The data are plotted in the above way in Figure 11 (for solutions containing no added PbCl₂) and in Figure 12 (for solutions in which PbCl₂ was added).

It is observed that irradiation has no effect in the former case, but affects the growth rate in the latter. This is exactly the opposite of the effect of irradiation on dislocation densities. The two effects are summarized in Table 1.

Effect of γ-Irradiation on the Crystal Growth rate from Solutions Containing No Added PbCl₂. The absence of any effect of irradiation on the growth rate in this impurity level ( \( \sim 10^{-8} \) moles PbCl₂/mole KCl) could be interpreted either (1) the mass transfer process through


TABLE 1

Summary of the Effect of $\gamma$-Irradiation on KCl Crystal Growth

<table>
<thead>
<tr>
<th>Concentration of PbCl$_2$ in Solution Moles/Mole KCl</th>
<th>Effect of $\gamma$-Irradiation On Dislocation Density</th>
<th>Effect of $\gamma$-Irradiation On Growth Rate of (100) Faces</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sim 10^{-8}$ (No added PbCl$_2$)</td>
<td>Reduces Dislocation Density</td>
<td>No Effect</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>No Effect</td>
<td>Decreases Rate</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>Crystals not Etched</td>
<td>No Significant Effect</td>
</tr>
</tbody>
</table>

the liquid was the controlling rate or (2) the $\gamma$-irradiation did not affect the surface resistance, i.e., the rate of attachment of the solute atoms at the crystal surface.

However, under the conditions of the above growth experiments, i.e., stirring rate higher than 850 rpm and growth rate lower than 150 $\mu$ hr, the liquid mass transfer resistance is not significant (see Section 4c). Therefore,
the second only of the above possibilities could be true.

The absence of any effect of radiation on growth rate is not contradictory to the reduction of the dislocation density by the irradiation. According to the dislocation growth theory, only screw dislocations are important for the crystal growth process. It appears, however, that γ-irradiation reduced only the density of the edge dislocations, since only edge and not screw dislocations can climb.

Effect of γ-Irradiation on the Growth Rate from Solutions in which PbCl₂ was Added. It is concluded from Figure 12 (curve A) that γ-irradiation decreased the growth rate of the (100) KCl faces in solutions containing \(10^{-7}\) moles PbCl₂/mole KCl. The reduction, however, of the growth rate in solutions containing \(10^{-6}\) moles PbCl₂/mole KCl does not appear to be significant, at least for growth rates (without irradiation) up to 125 µ/hr. (See Figure 12, curve B.)

It is suggested that an increase in the concentration of lead at the surface of the growing crystal under irradiation is responsible for the observed reduction in growth rates.

The hypothesis can be made that such an increase results from the following mechanism: γ-irradiation increases the diffusion rate of the lead in the bulk of the crystal towards the surface. The lead diffuses towards
the interface since, as it was assumed in Section 6, it is included in the crystal in concentrations higher than the equilibrium.

In solids the diffusion takes place mainly via defects, namely vacancies and interstitials. γ-irradiation produces a large number of such defects in a KCl crystal. Enhancement of the rate of diffusion is, thus, probable.

The suggested mechanism can provide a possible explanation of why γ-irradiation does not affect the growth rate in solutions containing no added PbCl₂. In this case the vacancies created by the γ-rays were "consumed" in the assumed above dislocation climb process. Thus, no enhancement in the diffusion rate of lead in the crystal would be expected. A dislocation climb didn't take place in crystals grown from solutions containing 10⁻⁷ moles PbCl₂/mole KCl.

The above mechanism can also provide a qualitative explanation of the shape of curve A, in Figure 12. It predicts that the slope of this curve would decrease appreciably at growth rates (without irradiation) of about 60 to 70 μ/hr., which is in agreement with the data. In addition, it indicates that the slope of curve B (Figure 12) would start decreasing only at growth rates of about 130 μ/hr. This means that if the suggested mechanism is correct, the effect of radiation on the
growth rate in solutions containing $10^{-6}$ moles Pb/mole KCl would have been observed with crystals grown at a rate higher than 130 $\mu$/hr. Attempts, however, to grow crystals at this growth rate region failed due to the formation of a large number of crystal nuclei in the solution.

6. DISCUSSION - INCORPORATION OF IMPURITIES DURING KCl CRYSTAL GROWTH (WITHOUT IRRADIATION)

a) State of the Art

Purification by recrystallization from an impure solution is predicated on the assumption that the solubility of impurities in the solution is greater than in the crystal. In crystallization practice, this assumption is almost always made. Radiochemists, however, working with radioisotopes have found that the effective distribution coefficient, $k_{\text{eff}}$, defined as ratio of the impurity concentration in the crystal to the concentration in solution, were, for certain impurities, greater than unity at low solution concentrations. Cases reported are:

(a) lead in alkali halides ($^{85,102}$) ($k_{\text{eff}}$ varied for each halide from 10 to 60, for KCl $k_{\text{eff}} = 57$), (b) lead and radium in alkali sulfates ($^{85}$), and (c) cadmium in sodium chloride ($^{18}$). It was also found that lead in sodium chloride was incorporated in the (100) but not in the (111) faces ($^{19}$).

In such studies the crystals were grown by cooling
or evaporating a saturated solution with little or no stirring. Under these conditions, the supersaturation, the temperature, and the concentration of the impurity in the solution were not constant. In addition, the diffusion of the impurity metal ions towards the crystal may have controlled the amount of metal incorporated in the crystal.

In the present investigation, in order to obtain meaningful results, the crystals were grown under carefully controlled conditions of temperature, supersaturation and impurity concentration in the solution. (See experimental procedure in Section 3a.) No irradiation was used in this part of the investigation.

b) Incorporation of Lead in KCl Crystals

Experimental results and their validity. The potassium chloride crystals, which were analyzed for lead content, consisted of two parts: that belonging to the original seed crystal, and the grown part.

From the lead content of the whole crystal (which was obtained from the analysis - see Section 3c), the lead concentration in the grown part of the crystal was calculated by knowing the weight of each part and the concentration of lead in the seed. The calculated values are summarized in Table 2, together with the experimental conditions under which each crystal was grown.

An uncertainty was introduced in the above calculation
## TABLE 2

**Lead Content of KCl Crystals Grown from Solution**

<table>
<thead>
<tr>
<th>Conditions of Crystal Growth</th>
<th>Concentration of Lead, moles/mole KCl</th>
<th>Effective Distribution Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Super-saturation %</strong></td>
<td><strong>Stirring Rate RPM</strong></td>
<td><strong>Growth Rate of (100) Face, μ/hr.</strong></td>
</tr>
<tr>
<td>0.16</td>
<td>1000</td>
<td>Dendritic</td>
</tr>
<tr>
<td>0.06</td>
<td>1000</td>
<td>52 ± 2.5</td>
</tr>
<tr>
<td>0.09</td>
<td>1000</td>
<td>57 ± 1.5</td>
</tr>
<tr>
<td>0.26</td>
<td>850</td>
<td>6 ± 1.0</td>
</tr>
<tr>
<td>0.32</td>
<td>850</td>
<td>15 ± 5.0</td>
</tr>
<tr>
<td>0.35</td>
<td>850</td>
<td>25 ± 7.5</td>
</tr>
<tr>
<td>0.38</td>
<td>1100</td>
<td>25 ± 7.5</td>
</tr>
<tr>
<td>0.38</td>
<td>850</td>
<td>27 ± 7.5</td>
</tr>
<tr>
<td>0.38</td>
<td>400</td>
<td>27 ± 7.5</td>
</tr>
<tr>
<td>0.44</td>
<td>1100</td>
<td>42 ± 7.5</td>
</tr>
<tr>
<td>0.44</td>
<td>850</td>
<td>42 ± 7.5</td>
</tr>
<tr>
<td>0.44</td>
<td>650</td>
<td>76.5 ± 12.5</td>
</tr>
<tr>
<td>0.44</td>
<td>400</td>
<td>101 ± 12.5</td>
</tr>
<tr>
<td>0.51</td>
<td>850</td>
<td>Dendritic</td>
</tr>
<tr>
<td>1.60</td>
<td>900</td>
<td>52 ± 2.5</td>
</tr>
<tr>
<td>2.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
by the impurity content of the seed crystal. As noted earlier, these seed crystals were cleaved from a larger melt crystal. Unexpected variations in the impurity level of the melt crystal were found, i.e., it was found to be inhomogeneous. It can be shown that these impurity variations would not affect significantly the magnitude of the final value of the impurity concentration in the grown crystal. They can account, however, for the observed scattering of the data.

Another factor contributing to the over-all error is the difficulty in measuring the small weight of the grown part, as it is obtained as the difference between two large numbers: the weight of the crystal before and after growth. This contribution to the error is presented in Table 2 as the "estimated percentage error".

The precision of the analytical method was checked by making two or three impurity-level determinations on samples taken from the same grown crystal. The average percentage deviation among these determinations was about 11%.

The effect a) of the concentration of lead in the solution and b) of the crystal growth rate upon the concentration of lead in the crystal will be discussed next.

Crystal lead concentration as a function of the solution lead concentration. Table 2 shows that the concentration of lead in the KCl crystals ranged from $21 \times 10^{-6}$ moles/mole KCl for the most dilute solutions up to $280 \times 10^{-6}$ for the solution of $10^{-5}$ moles PbCl$_2$/mole KCl.
The corresponding effective distribution coefficient $k_{\text{eff}}$ ranged from 2700 to 28. There is a scattering in the values of the distribution coefficients shown in Table 2 for each lead concentration in the solution. For instance, for a solution concentration $0.1 \times 10^{-6}$ moles Pb/mole KCl, $k_{\text{eff}}$ varies from 560 to 1680, depending on the growth rate of the crystal. Nevertheless, there is a definite qualitative trend, indicating that the distribution coefficient decreases with an increase in lead content of the solution.

The work of Yamamoto [180] indicates that at high lead solution concentrations $k_{\text{eff}}$ has values smaller than unity. From his data it also appears that the "azeotropic" crystallization concentration for lead (i.e., $k_{\text{eff}} = 1$) was about $10^{-3}$ moles PbCl$_2$/mole KCl; this is the concentration of lead in the crystal which cannot be reduced by further recrystallization in the conventional manner.

Kading [102] has reported the distribution coefficient for the system Pb-KCl to be 57 and quite independent of the experimental conditions and for all impurity concentrations in the solution up to $10^{-4}$ moles PbCl$_2$/mole KCl. However, his experimental conditions were different than the conditions of this investigation. First, his crystals were produced in an unstirred solution, and second the lead concentration was not kept constant during each run.

Variation of the Crystal Lead Concentration with the Crystal Growth Rate. The concentration of lead in the
grown KCl crystal as a function of the growth rate (only the rate of the (100) faces was actually measured) is plotted in Figure 13 for the constant lead concentration in the solution of $10^{-7}$ moles/mole KCl.

In spite of considerable scattering (due probably to the variation in the lead content of the seed crystal), there is a decrease in the lead content as the growth rate increases.

To explain the relationship between the crystal impurity concentration and growth rate, consider the following idealized case, which is based on Hall's model for the impurity incorporation in crystals grown from melt (86). At very slow growth rates, the concentration of the impurity in the crystal approaches some equilibrium value, $C_0$, which is a constant for any crystal-impurity system. $C_0$ values for the Pb$^{++}$ - KCl system are not, however, known. The surface concentration, $C_s^o$, is not equal to $C_0$ even in this limiting case, and $C_0 < C_s^o > C_L$, where $C_L$ is the liquid bulk concentration value.

As the crystal grows, the surface layers (at a concentration $C_s^o$) are covered, and the net concentration in the crystal exceeds $C_0$. This sets up a diffusion gradient inside the crystal which tends to decrease the crystal concentration towards $C_0$. At very slow growth rates, the impurity of a top layer would have sufficient time to diffuse to the interface before this layer is covered by a
subsequent one.

As the growth rate increases, the impurity would have less and less time to diffuse to the interface, and the concentrations in the bulk of the crystal would become larger than $C_0$. This increase in impurity concentration with increasing growth rate has been confirmed experimentally in crystals grown from melt (10,86). In addition, it has been treated analytically by Chernov (50), who found a relation similar to that shown by curve (1) in Figure 14. He showed that the upper part of the curve, where the impurity concentration remains constant, corresponds to growth rates $R$, such that $R \gg D_1/h$ where

$$D_1 = \text{the diffusion coefficient of the impurity ions in the crystal}$$

and

$$h = \text{the thickness of each deposited layer.}$$

However, let it be assumed now that the surface impurity concentration is not $C_s^0$, but it has a value $C_s < C_s^0$; this value depends on the time a crystal surface remains exposed to the solution, i.e., on the crystal growth rate. Thus, the impurity concentration at the surface is a decreasing function of the growth rate. This is expressed schematically by the curve (2) in Figure 14. The two curves (1) and (2), if combined, give the curve (3),
which expresses now the dependence of the impurity concentration in the bulk of the crystal upon the growth rate. Whereas for \( R \gg D_{f}/h \) in curve (1) the surface impurity concentration remained constant, in curve (3) it decreases as the growth rate increases.

In the present investigation, it is indeed \( D_{\text{Pb}^{++}}/h \ll R \). More specifically, \( D_{\text{Pb}^{++}} = 3.8 \times 10^{-19} \text{cm}^2/\text{sec} \) (by extrapolation to \( 35^\circ \) of the data by Glasner et al. (81)) and \( h \approx 25 \text{Å}^{0}(153) \); \( D_{\text{Pb}^{++}}/h \) is equal to \( 1.5 \times 10^{-12} \text{cm/sec} \), while the slowest growth rate is five orders of magnitude larger, i.e., 6 µ/hr or \( 1.7 \times 10^{-7} \text{cm/sec} \). Therefore, the growth rate studies in the present investigation correspond to the tail end of the curve(3) in Figure 14, and the crystal impurity decreases as the growth rate increases.

In the present system the impurity concentration-growth rate dependence indicated by the left side of the curve (3) might be observed at temperatures high enough for the ratio \( D_{\text{Pb}^{++}}/h \) to become of the same magnitude or larger than \( R \); for instance, at \( 150^\circ \text{C} \), \( D_{\text{Pb}^{++}}/h = 1 \mu/\text{hr} \). Obviously this condition is practically unattainable for aqueous solutions at atmospheric pressure.

One possible way to increase \( D_{\text{Pb}^{++}} \) without increasing the temperature is the use of \( \gamma \)-radiation. The possibility that \( \gamma \)-irradiation creates enough vacancies to increase the diffusion coefficient of the lead in the lattice was
discussed in Section 5. It is recommended to repeat the study of impurity concentration as a function of the growth rate inside a γ-radiation field.

c) Uptake of Other Impurities by KCl Crystals

The uptake by the KCl crystals of other impurities besides lead was also studied, namely the following ions were used: Fe^{+++}, Ti^{+++}, Bi^{+++} and Hg^{++}. The results are summarized in Table 3.

**TABLE 3**

Uptake of Impurities by KCl Crystals

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Concentration of the Impurity (moles/mole KCl)</th>
<th>Effective Distribution Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In the Solution</td>
<td>In the Crystal</td>
</tr>
<tr>
<td>Fe^{+++}</td>
<td>1 x 10^{-6}</td>
<td>325 x 10^{-6}</td>
</tr>
<tr>
<td>Ti^{+++}</td>
<td>1 x 10^{-6}</td>
<td>Not Detected</td>
</tr>
<tr>
<td>Ti^{+++}</td>
<td>10 x 10^{-6}</td>
<td>200 x 10^{-6}</td>
</tr>
<tr>
<td>Hg^{++}</td>
<td>10 x 10^{-6}</td>
<td>Not Detected</td>
</tr>
<tr>
<td>Bi^{+++}</td>
<td>10 x 10^{-6}</td>
<td>Not Detected</td>
</tr>
</tbody>
</table>
d) Engineering Consequences

Literature references to the phenomena of large impurity distribution coefficients are rare. Their importance has not been adequately recognized. The important practical consequences of the phenomena for the recrystallization and purification processes are the following:

1) Limits in the Purification by Recrystallization

It was shown above that the impurity distribution coefficient $k_{\text{eff}}$ in certain cases increases as the solution concentration decreases and becomes finally greater than unity; this indicates that there is a limit to purification by recrystallization. The solution concentration at which $k_{\text{eff}}$ becomes larger than unity is the average impurity concentration in a crystal which cannot be reduced further by recrystallization.

Actually when $k_{\text{eff}} > 1$ recrystallization does not remove the impurity, but concentrates it strongly in the first crystals precipitated.

2) Inhomogeneous Lead Distribution in KCl Crystals during Crystallization

Using the distribution coefficients obtained in this investigation (actually the average distribution coefficients for each solution concentration of the impurity), the fraction of PbCl$_2$ precipitated as a function of the fraction of KCl crystallized can be calculated. In Figure 15 the fraction of PbCl$_2$ remaining in solution vs.
the fraction of KCl crystallized is presented; the initial lead concentration was taken as $1 \times 10^{-6}$ moles/mole KCl.

The curve shows an extremely strong separation of lead in the first fractions; the 99.9% of the lead will be contained in the first 1.25% of the crystallized KCl.

Thus, in a batch crystallization of KCl, if the first crystals grown are not rejected, the distribution of Pb (and also Fe) among the various crystallites should be extremely inhomogeneous.

This was confirmed experimentally to be the case with the "Baker analyzed" reagent KCl. A certain number of crystallites from each reagent bottle were analyzed spectrographically for Pb and Fe. While the average lead concentration was 0.03 ppm, certain crystallites contained as high as 30 ppm lead. The same was true for Fe.

3) Production of Very Pure KCl and NaCl

Since the first crystals grown from a solution of KCl (and also NaCl) contain most of the lead, those which crystallize later will be of higher purity than the original KCl. Thus, rejection of the first crystal fraction should lead to very pure KCl and NaCl crystals.

There is a considerable need for such high purity reagent for the growth of large NaCl and KCl crystals from melt. The latter are used extensively for various
physical measurements, for instance to measure luminescence or to study the effect of irradiation on ionic crystals. Egli and Johnson (63) recently complained that "there is no commercial source for such a common substance as NaCl that will produce satisfactory crystals for physical measurements; ... the reagents contain enough lead and various other ions to have a measurable effect on impurity-sensitive properties".

In conclusion, in cases where distribution coefficients greater than unity are present, modification of the conventional techniques to include rejection of the first crystals grown (which would act to remove impurities from solution) is suggested.
FIGURE 1
SCHEMATIC DIAGRAM OF EQUIPMENT

FIGURE 2
SCHEMATIC DIAGRAM OF RADIATION SOURCE

FIGURE 3
EFFECT OF SUPERSATURATION AND PbCl₂ CONCENTRATION ON (100) FACE GROWTH RATE
**Figure 4**
KCI Growth Rate vs Stirring Rate
(NO PbCl₂ Added)

**Figure 5**
KCI Growth Rate vs Stirring Rate
(PbCl₂ Added)

**Figure 6**
Crystals grown at various stirring rates in the same solution

Supersaturation: 0.43%

PbCl₂ Conc.: 10⁻⁷ moles/mole KCl
FIGURE 7
COMPARISON OF MATCHED CLEAVAGE FACES
(MIRROR IMAGE)

Border between seed and grown region, ± 10μ
(Calculated from the growth rate measurements)

FIGURE 10
ETCHED SURFACE OF CRYSTALS GROWN
UNDER IRRADIATION (NO PbCl₂ ADDED)
(Part of Area of Picture 11 in Fig. 9)

FIGURE 8
DISLOCATION DENSITIES IN THE
GROWN PART OF A CRYSTAL vs
DISLOCATION DENSITY OF THE SEED
**Figure 13**
Concentration of Pb**⁺⁺** in crystals vs growth rate of (100) faces.

**Figure 14**
Variation of impurity concentration in the crystal with growth rate:
1. Hall's theory only
2. Variation of surface impurity concentration with growth rate
3. Combination of both effects

**Figure 15**
Amount of PbCl₂ remaining in solution vs amount of KCl crystallized.
FIGURE 9
ETCH PIT PATTERN IN GROWN CRYSTALS

A: Border between seed and grown region (calculated from the growth rate measurements, accuracy ± 10μ)

LEGEND

<table>
<thead>
<tr>
<th>Picture</th>
<th>PbCl2 added</th>
<th>Irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. moles/mole rad/min</td>
<td>KCl</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>2400</td>
</tr>
<tr>
<td>12</td>
<td>10^-7</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>10^-7</td>
<td>2400</td>
</tr>
</tbody>
</table>

FIGURE 11
GROWTH RATE OF (100) FACES UNDER IRRADIATION (Ri) VS GROWTH RATE WITHOUT IRRADIATION (R0)

NOTE: RATE VARIES DUE TO "NATURAL" IMPURITIES

FIGURE 12
GROWTH RATE OF (100) FACES UNDER IRRADIATION (Ri) VS GROWTH RATE WITHOUT IRRADIATION (R0)
CHAPTER 2

INTRODUCTION

Crystal growth has been always a topic of considerable interest for Chemical Engineers. In many chemical industries, like the sugar industry, the pigment industry, the organic chemicals and the inorganic salts industry, the product is either precipitated from a solution as a crystalline solid or is recrystallized from a solution for the purpose of purification. In most of the cases the utility and many properties of the final crystalline product are often largely determined by features such as crystal size, shape, uniformity, degree of perfection, size distribution and purity. In spite, however, of the great importance of crystallization processes, no general theory has been successful in explaining all aspects of crystal growth. In recent years the kinetic processes involved in crystallization have been clarified considerably. Partially successful theories have already been developed starting with Frank in 1949 (69), who put forward a structure sensitive theory of crystal growth. However, these theories were mainly developed for growth from vapor and they are usually extrapolated qualitatively to include growth from solutions. Experimental evidences and data are needed, therefore, to test the postulates of these theories, regarding growth from solution. In addition much remains to be done in explaining the often drastic effect of trace amount of impurities on the growth rate and habit of crystals growing from solution. The mechanism by which these additives or impuri-
ties act is not yet fully understood, although it is of great importance not only because additives have been used extensively in industry to modify crystal habit and facilitate control of the crystal growth but also because impurities are present even in the crystallization from what is considered as pure solution.

Another point needing clarification is the incorporation of the additives or impurities into the growing crystal, and more specifically the amount of impurity incorporated, the mechanism of incorporation and finally the relation between the impurity uptake and the effect of the impurity on crystal growth rate. The experimental data on this subject are very scarce although interesting theoretical treatments have been published recently (50).

The present investigation originated with the purpose to investigate the crystal growth process by using gamma radiation as a tool. The approach involved the measurement of potassium chloride crystal growth rates in a supersaturated solution. Four series of experiments were conducted; the first in a solution containing only the impurities inherent in the reagent grade potassium chloride, and the second series in a solution in which small amounts of PbCl₂ had been added. The other two series involved the same growth experiments as in the first two series, however they were carried out in a gamma-radiation field.
The results obtained under gamma-irradiation were analyzed by comparing with the results of identical experiments without irradiation. The results of the runs without irradiation were also analyzed by themselves alone and any valuable information concerning the mechanism of crystal growth and of impurity incorporation was extracted.

The idea of using high energy irradiation originated from the fact that irradiation of crystals will introduce defects in the crystalline lattice - namely point defects (vacancies-interstitials) and probably line imperfections (dislocations) - and may thus affect the structure sensitive crystal growth process. Moreover it is well known that irradiation has an effect on phase transition processes such as the formation of liquid droplets in a supersaturated vapor (Wilson's Chamber) or the nucleation and growth of vapor bubbles in a superheated liquid (bubble chamber).

Glasser (92) in his paper on bubble chambers predicted that ionizing radiation may have an effect in other phase transition processes like the nucleation in supercooled liquids and the nucleation and growth of crystals from supersaturated solutions.

It should be emphasized that in our experiments the crystals were irradiated while they were growing. There is only one such case of crystals irradiated during their growth reported in the literature. Kumar(113) used x-rays to irradiate potassium chloride crystals growing from a solu-
tion and studied only the effect of irradiation on the density of the crystals. He found that the density of these crystals was considerably less than the reported values for melt crystals. Similar experiments, using gamma-radiation were carried out as a secondary study of the present investigation. Similar results were obtained, but a different explanation than Kumar's is offered. This part of the investigation has been already published (20).

The balance of the thesis is organized as follows: Chapters 3 to 5 are concerned with the survey of the literature and the discussion of results of previous investigations, which are pertinent to the present investigation. In Chapter 6 the experimental procedure, which was followed in this investigation is described. In Chapters 7 to 10 the results of the present investigation are presented and discussed. Each chapter deals with a certain phase of the investigation and is organized as follows: after a small introduction the experimental data are presented, then a discussion follows and the conclusions, regarding the particular system as well as the crystal growth in general, are drawn.

In the final Chapter 11, the conclusions and recommendations of the whole investigation are summarized.
CHAPTER 3
THEORY OF CRYSTAL GROWTH

3.1 General

The volume of the literature concerning the mechanism of crystal growth is extremely large (see \textsuperscript{11,163} for reviews). However, much of it is either speculative or contradictory probably because the available data were not always reliable. In recent years our understanding of many of the aspects of the growth process (including the reasons for the contradictory experimental data) has increased considerably through the development of the molecular-kinetic theories. These theories, however, have incorporated valuable concepts developed originally in some of the early theories. For this reason, a brief review of two of the older theories will precede the discussion of the molecular-kinetic theories.

3.2 Early Theories of Crystal Growth

3.2.1 Thermodynamic Theories

Many of the early ideas of crystal growth are based on the classic work of Gibbs on heterogeneous equilibria (\textsuperscript{79}). Curie in 1885 put forward the first theory of crystal growth. (\textsuperscript{54}) He assumed that crystal habit was determined only by thermodynamic equilibrium; that is, the predominant crystal form is the one possessing the minimum total surface free energy for a given volume of crystal. Wulff(\textsuperscript{179}) extending this theory indicated that Curie's statement implies that the rate of growth of a crystal face must be inversely proportional to the surface free energy of the face. This rela-
tion has been shown to hold in many cases but only qualitatively. Although the thermodynamic theories would explain the polyhedral habits of crystals, they were limited in scope, considering only the relative growth rates on different faces of a crystal and not involving the actual kinetics of growth. Moreover, Valeton (26,161), in considering Gibbs ideas, offered the main objection to these theories. He pointed out that the total free energy is inversely related to the linear dimensions of the crystal and therefore for crystals larger than one micron in size "the influence of surface energy on the equilibrium may be neglected."

3.2.2 Diffusion Theories

The diffusion theories (27) were developed almost as early as the thermodynamic ones. However, in contrast to the thermodynamic theories they treat crystal growth as a rate process. They consider diffusion of solute through a concentration boundary layer at the crystal surface to be the rate controlling mechanism for crystal growth. Historically the diffusion theories were developed as follows: Noyes and Whitney (138) put forward the simple expression representing a pure diffusion process

\[
\frac{1}{S} \frac{dx}{dt} = k(C_2 - C_0)
\]

(3-1)

where \(dx\) is the amount of material attached to the surface, \(S\) the surface area of the crystal, \(C_0\) the saturation con-
centration and \( C_2 \) the actual concentration. The assumptions in back of this relation are, of course, first that the rate of attachment of atoms to the surface is very fast relative to the rate of diffusion, and, second, that the concentration prevailing at the surface is at all times equal to \( C_0 \). This theory fails, like all diffusion theories, to explain why crystals grow as well formed polyhedra with plane faces and sharp edges. In addition however Noyes' theory did not explain why the growth rates differ from face to face. Three arguments were then invoked. Ritzel\(^{142}\) defended the view of different solubilities on the different faces, i.e. that \( C_0 \) is different for each face. Nerst\(^{134}\) on the other hand modified (3-1) by putting \( k = \frac{D}{\delta} \), where \( D \) is the diffusion coefficient and \( \delta \) the film thickness which, according to him may vary from face to face. Berthoud \(^{12}\) and Valeton \(^{162}\) investigate a third possibility: that the reaction at the crystal surface is not infinitely rapid, as assumed by the pure diffusion theories. Equation (3-1) was then modified to include the surface reaction resistance acting in series with the diffusional one:

\[
\frac{1}{S} \frac{dx}{dt} = \frac{1}{\delta/D+1/k_1} (C_2-C_0)
\]  

(3-2)

where \( k_1 \) the "coefficient of crystallization velocity" in the relation

\[
\frac{1}{S} \frac{dx}{dt} = k_1 (C_1-C_0)
\]

(3-3)
$C_1$ is the concentration at the surface, which is not the equilibrium concentration anymore, but it has a value such that $C_2 > C_1 > C_0$. According to Valeton $k_1$ in (3-3) is independent of concentration and therefore ought to be the same whether $C_2 > C_0$, i.e. growth, or $C_0 > C_2$, i.e. dissolution. This "reciprocity" of the growth and dissolution processes, however, has not been observed experimentally. It has been actually observed by many investigators that crystals often dissolve at a much higher rate than they grow (28). Moreover, if $k_1$ is independent of supersaturation, it can be shown easily that the relative rates of growth at the various faces, upon which the habit of the crystal depends, should be independent of the supersaturation. However, it is well known that a change in the degree of supersaturation often brings about a change in the habit of the crystals. Some other rather unlikely modifications were proposed to account for the dependence of the habit upon the supersaturation. The vagueness resulting from all these modifications became the main objection against diffusion theories.

Although bulk diffusion alone may be considered insufficient to explain the observed growth phenomena, diffusional processes are inevitably involved in crystal growth. For instance, it is realized that due to the presence of a diffusional layer of some thickness, supersaturation at the surface
is not necessarily the same as in the bulk of the solution. Diffusional resistances can impose a restriction to the growth of a crystal in some cases, for example, at a low degree of agitation. The experimental facts however point to the existence of an additional surface resistance, which becomes the controlling one at high solution velocities across the crystal surface. In this case the growth becomes essentially independent of liquid velocity, a fact which has been observed experimentally (48). The question regarding the nature of this surface "reaction" or surface attachment resistance or to put in another way the question, what is the precise significance of the factor $k_1$ in Equation (3-2) is answered by the molecular-kinetic theories, which will be considered next.

3.3 Modern Theories of Crystal Growth - Growth of Perfect Crystals

The early theories of crystal growth did not take into account (nor could they at the time of their development) the actual atomic arrangements at the crystal surfaces. However, with the development of crystal structure theories, a great deal of effort has been expended to associate the known characteristics of crystal growth with the prevailing crystal structure ideas. It was then recognized that molecular events occurring at the surface of the crystal are the most important factors in determining the growth of the crystal. This led the theoretical developments towards two directions: the adsorption layer theories and the molecular
kinetic theories.

The molecular kinetic theories are based on the fine structure of the crystal surface and have proved the most successful. The adsorption layer theories, which did not consider the fine structure of the surfaces, attempted to describe only what was happening at the surface before the crystallizing particles were incorporated into the lattice, and consequently they were not successful in explaining all the characteristics of crystal growth.

3.3.1 Adsorption Layer Theories

In 1922, Volmer (171) suggested that an adsorption step precedes the actual incorporation of the building units into the crystal lattice; i.e., the crystallizing particles upon arriving at the surface lose a portion of their latent heat (approximately one-half) and form an adsorbed layer. This layer is assumed by Volmer to be always in equilibrium with the solution and behaves like a two-dimensional gas. The adsorbed particles are free to move over the surface but occasional inelastic collisions between particles will result in the formation of the nucleus of a two-dimensional crystal. This crystal would attach itself to the lattice plane below and proceed to spread over the crystal surface. Volmer further assumes that the spreading velocity is proportional to some power, $n$, of the concentration of the solute in the adsorbed layer. The concentration itself could be related to the adsorption potential $A$ through a Boltzmann expression.
\[ C = v e^{A/kT} \]  
\( (3-4) \)

where \( v \) = a frequency factor 
\( k \) = Boltzmann constant 
\( T \) = absolute temperature

Volmer assumed the spreading velocity to be the controlling resistance in growth of a face. Therefore, if \( R \) is the growth rate normal to a face

\[ R \sim aC^n \sim ae^{nA/kT} \]  
\( (3-5) \)

where \( n \) is a constant for a given face and \( a \) a "steric" factor.

The adsorbed layer theory was a step in the right direction and it was able to explain some observations which actually led Volmer in the development of his theory. For instance, Mier's observation (127) that the solute concentration very close to the surface of growing crystals, measured by optical refraction methods, was higher than the concentration in the bulk of the solution.* In addition Volmer (170) was able to interpret his results on the growth of mercury crystals from the vapor state at low temperatures. His co-workers (172,173) later presented more evidences to support a process of surface migration of solute molecules: A jet of mercury droplets was allowed to

*It should be noted that Mier's results are at least surprising, since the depth of a layer which would change the refractivity index would have to be distinctly greater than what is usually understood by an "adsorbed" layer.
impinge upon a benzophenone crystal. Benzophenone molecules dissolve into the mercury droplets, at the time the droplets are in contact with the crystal surface. The tip of the crystal diminished in size even when at a considerable distance from the steam of droplets. Although the adsorbed layer theory explains the above mentioned observations, it has some major shortcomings. For instance, if we assume that a Langmuir type isotherm relates the surface concentration to the bulk concentration, the growth rate $R$ of the crystal becomes proportional to some power of bulk solute concentration, whereas most of the experimental evidence indicates that growth rate is related to supersaturation and not to the actual concentration of the solute. In addition Volmer's treatment implies reciprocity of growth and dissolution, which is contrary to experimental data, as it was mentioned in Section 3.2.2.

In 1927 Brandes (21) presented a modification of Volmer's theory. He assumed the same model as Volmer, but he considered the formation of the two-dimensional nucleus within the adsorbed layer as the controlling resistance. He proceeded further to calculate the work of formation of this nucleus for any given degree of supersaturation, although not very successfully. However, his theory succeeded in directing the attention of many investigators to the notion of two-dimensional nucleation. Kossel, Stranski and others incorporated this concept into their molecular kinetic theories and the outcome was what today
is called two-dimensional nucleation theory of crystal growth.

3.3.2 Two-dimensional Nucleation Theory

A perfect crystal can be visualized as a perfectly ordered array of atoms or molecules. Consider now an incomplete layer, or step on the face of a perfect crystal (shown in Figure 3-1).

FIGURE 3-1
SITES OF ATTACHMENT ON A CRYSTAL SURFACE

A molecule or an atom may join the growing crystal in one of the following sites: 1/in site A starting a new layer,
2/in site B starting a new row and 3/in site C continuing an existing row. Stranski(159) and Kossel(110) calculated the "energies of attachment" $E_A$, $E_B$, $E_C$ at the three sites A, B, and C respectively, by considering nearest neighbors interaction. They concluded that for both polar and homopolar crystals, $E_C > E_B > E_A$. It is easier (energetically) therefore for a new molecule to attach itself to a step than to a face and much easier to attach itself to an incomplete row (i.e. it results in the lowest energy configuration). That means that the ideal growth (from an energetic point of view) is as follows: if a crystal initially has a step, or any number of steps on its surface, these steps will propagate to the extremities of the surface forming complete layers. The question is now how the steps are formed.

According to the two-dimensional nucleation theory - which was initiated by Stranski(159) and Kossel(111) and developed subsequently by a number of investigators (9, 43, 74) - in a perfect crystal new steps are provided by the formation of a monolayer island (or two-dimensional nucleus). This formation involves an activation energy and has been treated analytically by the above investigators in a manner analogous to that used to describe homogeneous three-dimensional nucleation of a new phase. The change in free energy associated with the formation of a two-dimensional nucleus is the sum of two effects; the volume free energy of the system is reduced as solute
passes from the supersaturated solution to the crystal, while the total surface free energy increases, due to the additional surface created at the edge of the nucleus.

Thus for crystal growth from a supersaturated solution we have:

Decrease \( \Delta F_1 = N(\mu_c - \mu_s) \)  

Increase \( \Delta F_2 = \sum \sigma_1 A_1 \)

\[ \sum A_1 \]

Sum \( \Delta F = N(\mu_c - \mu_s) + \sum \sigma_1 A_1 \)  

where \( N \) = number of molecules in the nucleus  
\( \mu_c \) = chemical potential of bulk crystal phase  
\( \mu_s \) = chemical potential of the crystallizing species in the supersaturated solution  
\( \sigma_1 \) = interfacial free energy for the edge \( i \) of the nucleus  
\( A_1 \) = surface area of the edge \( i \)  
\( \mu_s > \mu_c \), therefore \( \Delta F_1 < 0 \)

If we assume that the nucleus is circular with an average edge interfacial free energy \( \sigma \), then \( N \) and \( A \) can be expressed in terms of the radius \( \rho \) of the nucleus, the crystal molar volume \( V_c \) and the height of the growth step \( a \).

\[ N = \frac{\pi \rho^2 a}{V_c} \]  
\[ A = 2\pi \rho a \]  

(3-8a)

In addition the chemical potential can be expressed in terms of solution concentration (approximating for activity)
\[ \mu_S = RT \ln C \]  
(3-8b)

\[ \mu_C = \mu_{C_0} = RT \ln C_0 \]  
(3-8c)

where \( C \) = concentration of the supersaturated solution

\( C_0 \) = concentration of the saturated solution at the same temperature

\( \mu_{C_0} \) = chemical potential of the crystallizing species in the saturated solution.

Thus Equation (3-8) becomes

\[ \Delta F = \frac{\pi \rho^2 aRT}{V_c} \ln \frac{C}{C_0} + 2\pi \rho \sigma \]  
(3-9)

or if we define supersaturation \( S \) as the ratio \( C-C_0/C_0 \)

\[ \Delta F = - \frac{\pi \rho^2 aRT}{V_c} \ln (S+1) + 2\pi \rho \sigma \]  
(3-10)

Equation (3-10) is represented in Figure 3-2.
It is observed in this figure, first that an activation energy is involved and secondly that for a given supersaturation there is a critical nucleus radius, corresponding to the point the over-all free energy change starts decreasing. Only nuclei having reached that critical value $\rho_c$ can survive. The concentration of these critical nuclei is related to their corresponding free energy $\Delta F_c$ by the expression

$$n_c \propto e^{-\Delta F_c/RT} \quad (3-11)$$

The free energy $\Delta F_c$ can be calculated by setting the derivative of (3-9) with respect to $\rho$ equal to zero, to find $\rho=\rho_c$ and substituting subsequently the value of $\rho$ in (3-9) to obtain

$$\Delta F_c = \frac{\pi \sigma^2 a V_c}{RT \ln(S+1)} \quad (3-12)$$

To find now the rate at which these critical size nuclei are formed, a kinetic mechanism analogous to the one proposed by Becker and Doring (9) for the three-dimensional nucleation could be employed. Then

$$J = v n_c = v e^{-\Delta F_c/RT} \quad (3-13)$$

and from (3-12)
\[ J = \nu e^{\frac{\pi \sigma^2 a V_c}{R^2 T^2 \ln(S+1)}} \]  
(3-14)

where \( J \) = nuclei formed per unit time and unit area
\( \nu \) = frequency factor

One of the assumptions employed by the theory of two-dimensional nucleation growth is that completion of each layer is much faster than initiation of a new layer. Thus the growth of a crystal face is limited only by the rate of two-dimensional nuclei formation. Therefore

\[ R \propto J \propto e^{\frac{\pi \sigma^2 a V_c}{R^2 T^2 \ln(S+1)}} \]  
(3-15)

where \( R \) the growth rate of a crystal face

Equation (3-15) predicts two things: 1/that a plot of the logarithm of the growth rate versus \( 1/\ln(S+1) \) should give a straight line for any face, with a slope simply related to the square of the interfacial free energy, and 2/that the growth rate is an extremely sensitive function of supersaturation. As a result, there is a critical supersaturation below which the crystal growth rate is negligible. This critical supersaturation can be estimated by assigning reasonable values to the parameters involved in expression (3-15). This can be done for growth from vapor and estimations based on these values \((41, 71)\) indicated that for an appreciable growth of one layer per second a supersaturation not less than 25 per cent is required while 50 per cent or more is commonly necessary.
There are a few attempts in the literature to correlate experimental data by (3-15). Straight lines were obtained with plots made as outlined earlier, but the calculated interfacial free energies were unreasonably low making the application of the theory of two-dimensional nucleation questionable. For instance Muller (130), working with growth of adipic acid from aqueous solutions, obtained a value about 0.3 ergs/cm² for the interfacial free energy. This value is judged as extremely low.

There are instances, however, where the demand of Equation (3-15) for a very sudden increase in the rate of growth of a perfect crystal surface as supersaturation increases has been confirmed experimentally. And even in some cases this observed critical supersaturation was found to correspond to the theoretical one. It should be emphasized that all the experiments involved growth from vapor. Frank in 1952 (71) pointed out that Haward's (82) molecular beam experiments are in a remarkable agreement to the expectations of surface nucleation theory. In these experiments Haward observed no appreciable growth or evaporation from a film of HgI₂ unless the beam of the same material with which the film was bombarded was at least 40 per cent over- or undersaturated respectively. Later investigators worked with crystals in the form of filaments having diameters of a few microns, as well as whiskers. The unusually high mechanical strength suggests that these so-called whiskers are nearly perfect. Sears observations on
the growth of p-toluidine platelets\textsuperscript{(151)} and Hg, Zn, Cd, and Ag whiskers\textsuperscript{(149, 150)} are in good agreement with the prediction of two-dimensional nucleation theory. Vermilyea's\textsuperscript{(169)} experiments also showed the existence of a critical supersaturation for the growth of a perfect surface, such as the side faces of a small whisker. He conducted electrodeposition experiments with copper whiskers. The large whiskers (>10\mu in diameter) behaved like ordinary pieces of copper wire showing uniform growth at overvoltages of 10-15 mV. Small whiskers (~3\mu in diameter), however, showed no growth at overvoltages as high as 100 mV and started growing appreciably at about 120 mV.

It appears, however, that although there is a small number of instances verifying the existence of a high critical supersaturation, in the majority of the cases this has not been observed. Actually in practice, crystals grown from vapor show appreciable growth rates at supersaturation levels as low as 1 per cent or even less\textsuperscript{(164, 174)}. An explanation for this discrepancy was proposed by Frank in 1949\textsuperscript{(69)}. He pointed to the fact that real crystals are imperfect and suggested that the growth process is structure-sensitive and thus strongly affected by the imperfections of the crystal.

3.4 Imperfections in Crystals

An imperfection is any deviation from a perfect regular lattice or crystal structure. All actual crystals are in
some respect imperfect. Imperfections considerably affect a number of the important properties of solids; for instance diffusion through solids may be accelerated enormously by the presence of imperfections. Also as it was stated above, Frank first pointed out (69) that imperfections are important in many cases of crystal growth and even may be involved to some extent in all crystal growth phenomena.

Imperfections could be classified as follows:

a) Zero-dimensional or point imperfections (or defects as are usually called): vacancies, interstitial atoms, colour centers, vacancy pairs etc.

b) One-dimensional or line imperfections: dislocations.

c) Two-dimensional or surface imperfections: grain boundaries, stacking faults, the crystal surface.

d) Three-dimensional or volume imperfections: voids, inclusions of a second phase, etc.

However, the term imperfection is used usually to signify only the first two classes, namely point defects and dislocations. These will be treated in detail next.

3.4.1 Point Defects

The simplest imperfection is a missing atom or lattice vacancy. Another type of defect is the interstitial. This defect forms when an atom or ion occupies a position in the crystal which is not a lattice site. In many cases a vacancy or an interstitial can exist alone in a crystal.

In ionic crystals, however, the neutrality condition necessi-
tates for each vacancy either the existence of a vacancy of opposite sign or the presence of the missing ion in an interstitial position in the same crystal. Such a pair of vacancies of opposite sign is called a Schottky defect, while the pair of defects which is created by an ion shifted to an interstitial position leaving behind a vacancy is called a Frenkel defect.* It has been concluded on the basis of ionic conductivity studies and density measurements that in alkali halides the most common defects are Schottky type, while Frenkel defects are more common in silver halides (104).

A certain proportion of point defects always exists in thermal equilibrium in an otherwise perfect crystal. It is true that the introduction of defects requires a considerable amount of energy input. However, the introduction of point defects increases the entropy of a crystal to a large measure; by introducing a vacancy or an interstitial into a perfect lattice the possible number of distinguishable arrangements of atoms increases enormously (from 1 up to $10^{23}$ - which is the magnitude of number of atoms per cc). The result is that at elevated temperatures the free energy of the crystal may be reduced by the introduction of point defects. The thermal equilibrium concentration of a certain type of point defects in a crystal can be easily calculated (104). It is found to be

*Of course often the charge equilibrium may be achieved by the simultaneous presence of other kinds of defects, e.g. divalent foreign ions in material containing normally monovalent ions.
\[ n = N \exp\left(-\frac{E_v}{kT}\right) \quad (3-16) \]

Where \( N \) is the number of available ionic sites and \( E_v \) is the energy of formation of a point defect. In alkali halides, the formation of separated pairs of positive and negative ion vacancies is favorable and the expression (3-16) becomes

\[ n_p = N \exp\left(-\frac{E_f}{2kT}\right) \quad (3-17) \]

where \( E_f \) is now the energy of pair formation and \( n_p \) the number of vacancy pairs. In KCl where \( E_f = 2.4 \text{ eV} \) \((103)\), \( n_p \) at 350°C is about \( 7 \times 10^2 \text{ cm}^{-3} \). It is evident that \( n_p \) is very sensitive to the value of \( E_f \). If the value \( E_f = 2.1 \) suggested by other investigators \((175)\) is used \( n_p \) is found to be about \( 2 \times 10^5 \text{ cm}^{-3} \).

A special type of defect is the so-called color centers. These are lattice defects which selectively absorb light of certain frequencies. Many alkali halide crystals while normally are colorless under certain circumstances appear colored, i.e. they possess color centers. The simplest type of color center is one called an F-center. F-centers can be introduced to an alkali halide either by heating it in an excess alkali vapor or by ionizing irradiation; e.g. \( \gamma \)-irradiated KCl assumes a magenta color. An F-center has been identified with an electron trapped into a negative ion vacancy. The electron is provided by the ionization of the alkali atom on entering the lattice or by
ionization due to irradiation. There is evidence for a number of other types of centers bearing trapped electrons: $F'$, $R_1$, $R_2$, $M$, $V$ centers. However $F$-centers are the most important for alkali halides.

Other properties besides color which are affected by lattice defects include, specific gravity, ionic conductivity and diffusion.

a) Specific gravity. Production of Schottky defects in a crystal results in an increase in the volume with no increase in mass, lowering thus the density of the crystal. The production of Frenkel defects does not, at least to the first degree, change the volume of the crystal, and so the density remains unchanged.

b) Ionic conductivity. Defects play an important role in determining the ionic conductivity. It has been shown that increasing the number of vacancies (by the introduction of divalent ions in the lattice of an alkali halide) results in an increased ionic conductivity. That means that vacancies play a key role in the diffusion process associated with the ionic conduction.

c) Diffusion. Diffusion in crystalline solids can take place by several distinct atomic processes. These processes involve either atomic interchange or defect mechanisms. At the present time, however, it is generally accepted that diffusion in solids takes place mainly via defects, and primarily via vacancies ($36,156$). An atom, for instance, can jump from its lattice position into a
neighboring vacancy leaving a vacant site behind. Another atom can then jump into this vacant site, thus shifting the vacancy to a third position. In the simplest case which is the case of self-diffusion with only one atomic species present, what actually happens is the migration of the vacancy through the lattice. In the presence of a concentration gradient, the average drift of many vacancies will be directed in such a way that after sufficient time the required net transport of mass will have taken place.

The diffusion coefficient $D$ can be expressed as a function of temperature by the relation (57):

$$D = D_o C_v e^{-E_m/RT}$$

(3-18)

where $C_v = \text{atomic fraction of vacancies}$

$E_m = \text{activation energy for migration of a vacancy}$

$D_o = \text{constant}$.

Strictly speaking this relation applies to self-diffusion. Some minor changes are necessary in the case of the presence of a chemical concentration gradient, and especially in cases where an association probability exists between the diffusing atoms and vacancies. These associations may exist because the lattice distortions around the impurity atom are partially released by the presence of the vacancy. It was found that the migration energy of the complex is lower than that of the individual atom and the diffusivity is thus appreciably enhanced (100). Generally speaking,
however, we can state that the diffusion coefficient in a crystal is proportional to the vacancy concentration.

The equilibrium concentrations of vacancies at temperatures much lower than the melting point are not very appreciable, e.g., in KCl at $35^\circ$C there are 1400 vacancies per cm$^3$. However there are ways for the formation of vacancies and interstitials leading to high non-equilibrium concentrations. For instance even the most carefully prepared crystal of NaCl or KCl contains divalent or trivalent atom impurities. To ensure electrical neutrality a cation vacancy is introduced into the lattice with each divalent cation atom impurity. It is possible, therefore, that at moderate temperatures the number of vacancies present in such crystals is determined by the number of impurity ions rather than by the thermal equilibrium value.

Non-equilibrium concentrations of point defects may also be frozen into the solid by rapid quenching from a high temperature. In addition they can be introduced by plastic deformation and by high-energy irradiation. The production of defects by irradiation will be treated in detail in Section 5.

It was shown above that on raising the temperature of a crystal the concentrations of vacancies and interstitials that occur in thermal equilibrium increase and on lowering the temperature they decrease. The obvious question now is where the new defects come from or how do they
disappear. It appears that other lattice imperfections namely the dislocations, play an important role in this respect acting as sources and sinks for the lattice defects.

3.4.2 Dislocations

Originally the concept of dislocations was introduced in order to explain the weakness of crystalline solids and notably of metals. Since, direct evidences of their presence have been produced and it has been shown that dislocations are helpful in explaining crystal growth, electrical conductivity, and other phenomena as well.

Dislocations in contrast to point defects are regions of mismatch, in which the atoms are not lined up in a perfect array. To visualize a dislocation let us imagine that a perfect crystal (Figure 3-3(a)) was cut up to the line CD and the two parts were slipped in one case perpendicular to the line CD (Figure 3-3(b)) and in another case parallel to the same line (Figure 3-3(c)). In the first case an edge dislocation is produced and in the second a screw dislocation. The line CD indicating the boundary between the slipped and the unslipped regions is known as the dislocation line. The deformation produced in crystal (b), Figure 3-3, by the edge dislocation may be thought of as caused by inserting an extra plane of atoms on the right half of the crystal (see top face of the crystal). The genesis of a screw dislocation in crystal C, Figure 3-3, on the other hand transforms successive atom planes into a
FIGURE 3-3
DISLOCATIONS IN CRYSTALS
(a) Perfect Crystal
(b) An Edge Dislocation
(c) A Screw Dislocation
spiral ramp winding through the crystal around the dislocation line CD.

An alternative way to describe a dislocation is by means of a closed loop surrounding the dislocation line. This loop can be drawn by proceeding through the undisturbed region surrounding a dislocation in steps which are integral multiples of a lattice translation. The loop is completed by going an equal number of translations in a positive sense and negative sense in a plane normal to the dislocation line. Such a loop as it is shown in Figure 3-3(a) closes upon itself if it does not enclose a dislocation. However, it fails to do so if a dislocation is enclosed (as in crystals (b) and (c) of the same Figure) by an amount \( S \), called Burgers vector. This vector is used to characterize the type of a dislocation. It is perpendicular to the dislocation line in case of an edge dislocation, but parallel to the dislocation line in case of a screw type one. In general, however, a dislocation may be a curved line - and in most of the cases it is - i.e. the dislocation has neither pure edge nor pure screw character.

Such a dislocation can be always characterized by determining its Burgers vector, which now is at an angle with the dislocation line and it can be analyzed in a screw and an edge component.

Near the dislocation the crystal is highly strained. Less energy, therefore, is required to remove an atom from
the surface of the solid near the dislocation. This property is used by the etching technique in obtaining direct optical evidence of the presence of dislocations in crystals. By using suitable solvents, etch pits bounded by crystallographic planes can often be observed on metal surfaces. These etch pits indicate, though not uniquely always, sites where dislocation lines meet the surface.

The formation of the etch pits is explained in more detail in Appendix A, where also the etching technique developed for the present investigation is presented.

The origin of dislocations is as yet rather obscure. Dislocations, in contrast to point defects, cannot be present in thermal equilibrium, because their energy is very large in comparison with the increase in entropy that they produce. They must therefore be introduced in a non-equilibrium manner. Several theories as to the possible mechanisms of their formation have been proposed. During the solidification of crystals from the melt, the crystal becomes supersaturated with lattice vacancies. The excess vacancies condense to form flat disks, which in turn collapse to form dislocation rings. These rings grow with further vacancy precipitation.

The dislocations in crystals grown from solution are attributed to a number of possible mechanisms: propagation of dislocations already present in the seed, formation of dislocations during the accidental encounter of two nuclei in the case of homogeneous nucleation,
and, most important, introduction if dislocations by impurities (47,71).

3.4.3 Interaction Between Dislocations and Point Defects

Physical point defects (vacancies and interstitials) as well as chemical point defects (impurity atoms) are attracted by dislocations.

Impurity atoms tend to cluster around a dislocation. This can be understood physically as follows: atoms with a smaller or larger radius than normal lattice atoms will be accommodated better in those regions around a dislocation where the lattice is expanded or contracted. Generally speaking it can be said that there is a decrease of the free energy of the system when the impurity atom penetrates into the stress field of the dislocation (34). Not only elastic, but also electrical (Coulomb) interaction and chemical interaction (formation of molecules or even a second phase) may contribute to such an energy decrease.

A mutual interaction also exists between dislocations and vacancies or interstitials. In fact, a physical point defect can be absorbed on a dislocation and then lose its identity.

The simplest way to visualize such an elimination is illustrated in Figure 3-4. There at the end of an extra half-plane, which forms an edge dislocation, is a kink or jog. When a vacancy arrives next to a jog it can absorb the atom A. This results in the disappearance of the vacancy and the simultaneous displacement of the jog by one atomic
distance to the right. On the other hand the jog shifts one distance to the left when an interstitial is absorbed. Jogs thus act as sinks for point defects. Point defects once attracted to an arbitrary dislocation site, will migrate towards the nearest jog to be absorbed.

The reverse process, i.e. the emission of point defects by jogs can also take place. This is due to the fact that the atom at the corner of the jog is energetically not as stable as the others; it has only two nearest neighbors whereas all the other atoms along the edge dislocation have
three nearest neighbors in the extra plane. One of two things can therefore happen. The jog serves to attract another atom from the crystal - which leaves behind a vacancy -, or the corner atom leaves the extra plane to move into an interstitial position.

In thermodynamic equilibrium, emission of point defects by jogs takes place as frequently as absorption. When, however, the crystal is supersaturated or undersaturated in point defects a net absorption or emission takes place respectively. Thus, it is generally accepted nowadays that dislocations play an important role in equilibrating lattice defect concentration in crystals (128).

The interaction between edge dislocations and point defects is expected to be exceptionally strong in polar crystals, like alkali halides. There a jog has an effective charge, either positive or negative, and therefore, apart from the strong elastic interaction, an electrostatic interaction exists between edge dislocations and point defects (31).

3.4.4 Dislocation Climb

A dislocation can move either in its slip plane or normal to it. Motion on the slip plane is called glide, while motion normal to it is called climb. The latter will be described here.

Suppose that enough vacancies diffuse to the edge dislocation in Figure 3-4, so that the whole incomplete
row in the extra plane disappears. As a result, at point B, the edge dislocation will now lie on the next higher plane. That is the dislocation moved upwards by a shrinkage of the extra plane.

The opposite could happen if interstitial atoms diffuse to the edge dislocation. The extra plane grows and the dislocation moves downwards.

This dislocation motion is called climb. It is conventional to define the positive direction of climb as the direction for which atoms must be taken away (by vacancies) from the extra plane, so that the extra plane shrinks. In negative climb the extra plane grows (by the arrival of interstitials).

It is understood that if a great number of vacancies is available, the whole extra plane could disappear. It is said then that the dislocation "climbs out".

In case the dislocation line is not straight but a loop, climb would result in the decrease or increase of the dislocation loop length.

3.5 Growth of Imperfect Crystals

Two-dimensional nucleation growth theory was the first to give any consideration to the fine structure of the crystal. At the time of its development, however, the present understanding of the nature of the deviations from perfect crystals had not yet really begun. For this reason, the two-dimensional nucleation theory assumed a perfect lattice and a surface free of imperfections. This
led, as it has been pointed above, in a prediction of a high growth resistance of crystals, much higher than the one observed in crystallization practice.

An explanation for this discrepancy was proposed by Frank (62). He point out that a crystal containing a screw dislocation, (or more exactly a dislocation whose Burgers vector has a component normal to the face), has a surface which remains stepped, no matter how far the step advances. In other words, this step is self-perpetuating, and the need of two-dimensional nucleation never arises.

3.5.1 Growth from Dislocations - Qualitative Model

The step created by the dislocation will advance across the crystal surface the same as on a perfect crystal. A straight step (infinite radius of curvature) advances parallel with itself with a uniform velocity \( v_\infty \). The rate of advance of curved step is less than that of a straight step and it has been shown to be (42)

\[
\frac{v_\rho}{v_\infty} = v_\infty (1 - \frac{\rho_c}{\rho})
\]

(3-19)

where \( \rho \) is the radius of the curvature of the step and \( \rho_c \) is the radius of the critical two-dimensional nucleus for the supersaturation of the solution. Strictly speaking this relation is more nearly correct at low supersaturations and for values of \( \rho \) somewhat larger than \( \rho_c \). The reason for the decrease in velocity with curvature is a consequence of the fact that molecules attached at a
highly curved step have fewer neighbors than in a straight step and hence are held less strongly and have a higher solubility. For $\rho = \rho_c$ the rate of advance $v_\rho$ becomes zero.

The step created by a screw dislocation is initially straight and tends to advance across the surface with a constant linear velocity $v_\infty$. However, since the step is anchored at one end at the dislocation line, the angular velocity is greater near the dislocation line and decreased outward from it. As the step advances, therefore, it develops a curvature near the dislocation line (Figure 3-5), i.e. the inner sections will make initially more

![Figure 3-5](image-url)
revolutions per unit time than the outer sections.

Because of the increase in curvature, however, the inner sections will advance more slowly, in accordance with Equation (3-19). Eventually the curvature near the dislocation line will reach the value $\rho_c$ and the velocity of advance at that point will become zero. Then a steady state configuration of the growth spiral is obtained, the angular velocities of all parts of the step are the same, and the whole spiral rotates around the dislocation center with stationary shape. The spacing $y_o$ between successive steps of the spiral was calculated first by Frank (42). He assumed an Archimedean spiral and found

$$y_o = 4\pi \rho_c$$  \hspace{1cm} (3-20)

Cabrera and Levine (46) however considered the configuration of the spiral in more detail and obtained

$$y_o = 19\rho_c$$  \hspace{1cm} (3-21)

The growth of the crystal face can be viewed as occurring by rotation of the spiral. Every time the spiral makes one turn, the face advances by one step-heights. If $\omega$ is the angular velocity of the spiral, then $\frac{\omega}{2\pi}$ is the number of turns of the spiral per unit time. Therefore the rate of growth normal to the face is:

$$R = \frac{\omega}{2\pi}$$  \hspace{1cm} (3-22)
The number $\frac{\omega}{2\pi}$ shows also the number of new steps created in the unit time and it is termed the activity of the dislocation.

Although it is convenient to consider growth as occurring by rotation of the spiral, however the actual process is still a steady advance of each step in the plane of the surface. In other words dislocation growth theory shares the concept of layer growth, with the two-dimensional growth theory. According to this concept the growth of a crystal face can conveniently be considered in terms of a) the creation of steps at certain sources and b) their motion away from the sources.

In two-dimensional nucleation theory sources of steps are created by surface nucleation at any point on a perfect crystal surface. The growth rate, according to this theory is controlled only by the probability of the formation of the step. The subsequent advance of the step is extremely fast and is not a limiting factor in controlling the growth rate of the crystal face.

Dislocation growth theories, on the other hand, suggest that in real crystals sources of steps are always present. The entire kinetics of growth is then determined not only by the activity of the dislocation source, (i.e. the number of steps emitted from the dislocation center), but also by the motion and interaction of steps on the crystal surface (i.e. the velocity with which the steps
are advancing). Two quantitative models have considered this motion and interaction of steps: the one proposed by Frank (42) and the other by Hirth and Pound (94). These will be taken up shortly, but first the equilibrium structure of a stepped crystal surface will be considered.

3.5.2 Point Defects in the Surface and Their Mobility

It was shown in Section 3.4.1 that crystals contain a thermal equilibrium concentration of point defects; for instance the number of vacancies in a crystal at temperature T is

\[ n_v = N \exp\left( - \frac{E_v}{kT} \right) \]  (3-16)

where \( N \approx 10^{23}\text{cm}^{-3} \) is the number of available ionic sites and \( E_v \) is the energy of formation of a vacancy.

Similarly, it can be stated that atomically flat surfaces contain surface vacancies (Figure 3-6, position 2) and surface adsorbed atoms (Figure 3-6, position 1). Their surface concentrations are \( n_v^{(s)} \) and \( n_a^{(s)} \) respectively, and are given by formulas analogous to (3-16)

\[ n_v^{(s)} = N_s \exp\left( - \frac{E_v^{(s)}}{kT} \right) \]  (3-23)

\[ n_a^{(s)} = N_s \exp\left( - \frac{E_a^{(s)}}{kT} \right) \]  (3-24)

where \( N_s \approx 10^{15}\text{cm}^{-2} \) is the number of surface lattice posi-
FIGURE 3-6
POINT DEFECTS ON SURFACE AND STEPS

FIGURE 3-7
A STEP AT T = 0°K
tions, \( E_v^{(s)} \) the energy of formation of a vacancy at the surface and \( E_a^{(s)} \) the energy of "formation" of an adsorbed atom. (i.e. the energy to bring an atom from the bulk of the crystal to the surface) The latter is related to the energy of vaporization \( E \) and the energy of desorption \( E_d \) through the relation

\[
E = E_a^{(s)} + E_d
\]

Cabrera (45) argued that \( F_v^{(s)} < E_v^{(s)} \), which means that \( n_v^{(s)} > n_a^{(s)} \), i.e. the concentration of surface vacancies is higher than that of adsorbed atoms. In the same paper, he also indicated that the proportion of vacancies on the surface is substantially larger than in the volume.

The surface point defects can, obviously, play an important role in any transport process taking place on the surface. Their surface diffusion coefficients are:

for the surface vacancies

\[
D_v^{(s)} \sim a_v^2 \exp (- \frac{U_v^{(s)}}{kT})
\]

and for the adsorbed atoms

\[
D_a^{(s)} \sim a_a^2 \exp (- \frac{U_a^{(s)}}{kT})
\]

where \( v \sim 10^{12} \text{ sec}^{-1} \) represents some average of molecular frequencies and \( U_v^{(s)} \) and \( U_a^{(s)} \) are activation energies.
between neighboring equilibrium conditions on the surface; 
a is the distance between these positions.

The transport of matter along the surface could take 
place either by migration of the adsorbed atoms or by 
migration of the surface vacancies or both. In order to 
decide which of the above two types of migrations (sur-
face vacancies or adsorbed atoms) is the more important 
one should compare the two factors $n_v(s)D_v(s)$ and $n_a(s)D_a(s)$. 
It was indicated above that $n_v(s) > n_a(s)$, however it cannot 
be said that also $D_v(s) > D_a(s)$. Actually Cabrera has stated 
(45) that very likely it is $U_v(s) > U_a(s)$ and consequently 
from Equations (3-26) and (3-27) $D_v(s) < D_a(s)$. Therefore it is 
not possible to reach a general conclusion about the more 
important transport process. Cambrera, however, presumed 
that the current of adsorbed atoms is more important in 
pure surfaces. In presence of adsorbed impurities - he 
stated - the surface vacancies will be predominant in 
controlling surface transport. He did not give, however, 
any supporting evidence for his statement.

An important variable connected with the adsorbed 
atoms is the average mean displacement of an adsorbed 
atom $\lambda_s$, i.e. the distance diffused by an atom on the 
surface before evaporating (or going back into the solu-
tion). This can be defined by Einstein's formula (45)

$$\lambda_s^2 = D_a(s) \tau(s)$$  \quad (3-28)
where \( \tau(s) \) is the mean life of an adsorbed atom before being desorbed again from the surface, given by the relation:

\[
\tau(s) = \nu^{-1} \exp \left( \frac{E_d}{kT} \right).
\]

(3-29)

From vapor growth data (45) it appears that \( \lambda_s \) can have values between \( 10^{-6} \) to \( 10^{-3} \) cm.

3.5.3 Structure of a Monomolecular Step

Thermal fluctuations can create point defects in the surface of even a perfect crystal, but they cannot create steps on a close-packed* crystal surface (unless, perhaps close to the melting point) as it was shown by Burton and Cabrera (41).

A step, once formed either by a two-dimensional nucleation or a screw dislocation, will not be atomically smooth due to thermal fluctuations. Potential energy considerations show that at absolute zero a step is atomically smooth (Figure 3-7). As the temperature is raised, however, a certain number of edge vacancies (Figure 3-6, position 4) and a certain number of edge adsorbed atoms (position 3) as well as a large number of kinks (positions 5 and 6) appear. It was proved (42) that the concentration of adsorbed atoms and vacancies in the step is

*As close-packed is defined by Burton and Cabrera, a surface, if, when it is as flat as possible, all the surface molecules are at the same distance from a plane parallel to it (such a surface is the (100) face of NaCl). In all other cases the surface will present a stepped appearance.
small compared with that of kinks. Kinks result from the formation of groups of edge-adsorbed molecules or edge vacancies. According to Frenkel the proportion of lattice positions in a step occupied by kinks is proportional to $\exp(-w/kT)$, where $w$ is the energy of formation of a kink.

Cabrera and Coleman (44) calculated the mean distance $\lambda_0$ between kinks using $w = E/10$, where $E$ is the evaporation energy. They found $\lambda_0 = 4a$, i.e. one kink in every 4 lattice positions along the step.

It has been suggested first by Kossel(109) and accepted later by almost all investigators that during the growth new atoms are added to the crystal only at the kinks. The concentration of the kinks, as indicated above, is very high and consequently new atoms arriving at the surface are easily incorporated at the step. In other words, since $\lambda_s \gg \lambda_0$, any atom on the surface near the step will have a high probability to reach a kink before it is desorbed. Hence, the step can be regarded as a continuous line sink for the diffusing atoms. The velocity with which the step advances is determined by the rate of arrival of new atoms at the step. Therefore the problem of calculating the velocity of advance of a step becomes the problem of determining and measuring the controlling diffusional resistance. Two models have been suggested: a) Frank's in which the flux of atoms to a step is controlled by a bulk diffusion resistance and b) Hirth and Pound's in which
the surface diffusion resistance is the controlling step.

3.5.4 Frank's Model of Dislocation Crystal Growth

Frank applied his model both to growth from vapor and to growth from solution. Only the case of growth from solution will be considered here.

Frank (42) treated the solute diffusional problem in the following way: He assumed a model consisting of a set of parallel steps on a crystal surface at a distance \( y_0 \) from each other. As an approximation, he assumed three diffusional resistances in series: at distances less than \( \lambda_0 \) from the kink (\( \lambda_0 \) is the distance between successive kinks in each step) a hemispherical diffusion field exists around each kink; at distances between \( \lambda_0 \) and \( y_0 \) from each step a semi-cylindrical diffusion field exists around each step; and finally, at distances from the crystal surface between \( y_0 \) and \( \delta \) (\( \delta \) is the thickness of the unstirred boundary layer at the surface of the crystal) a plane diffusion field exists. Assuming equilibrium concentration at the kinks (i.e. zero supersaturation), Frank formulated equations describing the flux of solute atoms through each of the diffusion resistances. Equating, then, the fluxes, he eliminated the intermediate supersaturations at the boundaries of the in-series diffusion fields and he obtained the following expression.

\[
v_\infty = \frac{DC}{\lambda_0} \frac{2\pi S}{\lambda_0} \left[ 1 + \frac{2\pi a (\delta - y_0)}{\lambda_0 v_0} + \frac{2a_1 n_v}{\lambda_0} \right]^{-1} \quad (3-30)
\]
where \( V_\infty \) = the velocity of a straight step
\( Q = \) volume of a molecule of solute
\( D = \) diffusion coefficient of the solute in the bulk solution
\( C_o = \) saturation concentration in solution
\( \delta = \) thickness of the boundary layer
\( a = \) height of the monomolecular step

Frank also showed (as it was mentioned above) that

\[
y_o = 4\pi \rho_c \quad (3-20)
\]

Also assuming an Archimedean spiral he found for the angular velocity that

\[
\omega = \frac{v}{2\rho_c} \quad (3-31)
\]

\( \rho_c \) is the radius of the critical nucleus for the supersaturation S. Its value is (see Section 3.3.2)

\[
\rho_c = \frac{\sigma V_c}{RT \ln(S+1)} = \frac{\sigma V_c}{RTS} \quad (3-32)
\]

From Equation (3-30) one may determine the growth rate R of a crystal face as follows: the time interval between the pass of two successive steps from a certain point on the face, i.e. the time it takes for the step to advance in a distance \( y_o \), is \( y_o/v_\infty \). At the same time the crystal face has advanced in a perpendicular direction a distance \( a \).
Therefore

\[ R = \frac{v_\infty a}{y_0} \quad (3-33) \]

Combining Equations (3-30) and (3-33) the rate of growth normal to a face can be expressed as

\[ R = \frac{DC\Omega a2\pi S}{\lambda_0 y_0} \left[ 1 + \frac{2\pi a(\delta-y_0)}{\lambda_0 y_0} + \left( \frac{2a}{\lambda_0} \ln \frac{y_0}{\lambda_0} \right)^{-1} \right] \quad (3-34) \]

This equation could be simplified by estimating the relative sizes of the terms in the denominator. At low supersaturations \( y_0 \) is large (see Equations (3-20) and (3-32)) and the third term will dominate. On the other hand at high supersaturations \( y_0 \) will be small and the second term will dominate the terms inside the bracket.

Hence, for low supersaturations, by combining (3-34) with (3-20) and (3-32)

\[ R = \frac{DC\Omega RTS^2}{4\sigma V_{\infty} \ln y_0 / \lambda_0} \quad (3-35) \]

i.e. the growth rate is proportional to the square of the supersaturation (parabolic law of growth).

For high supersaturations we obtain

\[ R = \frac{DC\Omega S}{\delta} \quad (3-36) \]

i.e. the growth rate is proportional to the supersaturation (linear law of growth - see Figure 3-8).
FIGURE 3-8

THE GROWTH RATE AS A FUNCTION OF
SUPERSATURATION ACCORDING TO FRANK'S THEORY

(Logarithmic scale; see Ref. 42, p. 321)
It has been proposed that the transition from parabolic to linear occurs at about 0.1% supersaturation \(^{(42)}\), in the case of growth from solution. For growth from vapor the transition takes place at higher supersaturation: 1 to 10%.

The theory presented assumes only one dislocation to be present. Burton, Cabrera and Frank in their detailed theory of interactions between growth spirals indicated that the presence of more than two dislocations makes a remarkably little difference \(^{(42)}\).

Consider a pair of screw dislocations of opposite sign, i.e. opposite rotation. The two dislocations will create a step having both ends in the surface (in the case of a single screw dislocation the step starts on the surface but terminates on a boundary). If the supersaturation is zero, then the step will be straight. If the supersaturation is now raised, the step will start advancing. However, since it is anchored at both ends it will become curved (Figure 3-9). As the step advances the radius of curvature will decrease to a minimum value of \(\frac{r}{2}\) (where

![Figure 3-9](image-url)
r is the distance between the two dislocation lines) and then it will start increasing again. Hence the step will advance only if the supersaturation is equal or higher than the supersaturation corresponding to a critical nucleus radius to \( r_c = \frac{R}{2} \) (see Equation 3-32). For a given supersaturation, therefore, no growth occurs if the pair of the opposite sign dislocations is closer than \( 2r_c \).

It is obvious that a similar situation develops when an advancing straight step encounters two immovable obstacles spaced closer than \( 2r_c \). In this case the step will be held up. If the distance between the two obstacles (or the two dislocations) is greater than \( 2r_c \), then the step can pass between them, but since it acquires a curvature the velocity of advance would be reduced (see Equation 3-19).

Frank (42) considered the case of two screw dislocations of like signs. Based on topological considerations he concluded that if the two dislocations are separated by a distance large compared with \( 2\pi r_c \), the crystal surface is divided into two parts, which may be said to be fed with steps from each center respectively. In other words the growth rate is everywhere the same as if only one dislocation were present. The only difference would be that examination of the growing face would reveal two growth spirals. However, if two dislocations of the same sign are closer together than \( 2\pi r_c \), they behave
like a dislocation of double strength. They are called cooperating dislocations and they send out growth steps twice as fast as a single dislocation. Similarly the activity of a group of dislocations of the same sign, each a distance smaller than $2\pi p_c$ from its next neighbor is a multiple of the activity of a single dislocation. In some cases the multiplication factor can be as great as the number of dislocations contained in it. Increased activity means smaller distance $y_0$ between the steps produced by the above two or more dislocations of the same sign. According to Equation (3-33) the growth rate $R$ of the crystal should increase. However, the rate of advance $v_{oo}$ of the steps decreases when the distance between steps decreases, since the diffusion fields of the steps start interacting (more steps compete for the same number of diffusing atoms). The result is that $R$ cannot surpass the linear law (3-36) according to Frank (42). Thus, the growth rate in the regime of "high" supersaturation is not affected by the increase in the number of cooperating dislocations. In the regime of "low" supersaturation, however, which gives a parabolic law, the growth rate can be increased; this chiefly means, that the regime of the linear law (see Figure 3-8) is reached sooner.

It can be concluded, therefore that according to Frank's model, the linear law (Equation 3-36) represents the maximum attainable growth rate. Crystal faces having attained this rate cannot be made to grow faster by increasing the number of dislocations. On the contrary, the rate
could decrease slightly, if the dislocations introduced included pairs of opposite sign, closer together than \(2p_c\); such pairs can impose a small delay on the passage of steps originating elsewhere. Nevertheless, crystals growing at low supersaturation, where the growth follows the parabolic law (3-35), may grow faster when the number of dislocations increases; in this case the growth approaches the linear law (3-36), but it cannot surpass it (see Figure 3-8).

Besides the growth in the regime of the parabolic law another case can be visualized, in which an increase in the number of dislocations may result in an increased growth rate. Frank (42) pointed out that the observed rate of growth \(38,97\) in crystals is substantially lower than the linear low of his theory would suggest; occasionally a crystal does not grow at all, in spite of the fact that supersaturation is as high as 10%. A possible interpretation could be the excessive density of dislocations: i.e. the separation of dislocations of opposite sign is smaller than \(2p_c\). In this case, however, the number of dislocations per cm\(^2\) would have to be of the order of \(10^{12}\), which is very high for a crystal growing from solution. Frank, Cabrera, and Burton (42) are inclined to believe that inactivation by impurities of the dislocations present, or retardation of the step advance by adsorbed impurities (see Section 4), are the most rea-
sonable explanations. Impurities are present even in the crystallization from what is considered as pure solution. For a given concentration of impurities, it is obvious, that the larger the number of dislocations the greater the possibility that a certain number of them will remain active. In this case the growth rate would increase, attaining a value closer to the one predicted by Equation (3-34).

Moreover, it has been pointed out (73) that the adsorption of impurities is time dependent. This means that impurity adsorption rates and growth rates interact in an interesting manner. A fast growing surface may not have time to be poisoned and continuous to grow fast; but, if once stopped, it remains so. Thus, if somehow fresh dislocations could be produced continuously during the growth of the crystal and at a rate such that the impurities have no time to inactivate them, then the effect of impurities is minimized; the growth rate of the crystal would increase approaching the rate suggested by Frank for pure surfaces (Equation 3-34). As it will be explained in Chapter 5, high energy radiation could, under certain conditions, create dislocations in a crystal. Therefore, irradiation of a crystal during its growth, could introduce fresh dislocations continuously into the crystal and increase this way the growth rate of the crystal. This statement will be evaluated in the discussion of the results of the present investigation.
It should be emphasized, again, that in the preceding analysis, it was assumed by Frank that diffusion of the solute through a concentration boundary layer was controlling the rate of growth. The fact that in many cases the growth rate increases with increasing solution velocity supports this hypothesis. However, in many cases (48) (also in present investigation Section 7.1.3) it was found that, after a certain velocity of the solution relative to the crystal is attained, the growth rate becomes independent of the velocity. In those cases apparently another resistance becomes important. It has been suggested by a number of investigators, including Frank (42), that this resistance is the diffusion of the crystallizing atoms over the surface to the advancing step.

3.5.5 Growth with Surface Diffusion Resistance

Hirth and Pound (94,95) have suggested a model which considers the surface diffusion resistance to be the primary resistance in most instances of crystal growth and evaporation. Like Frank in the preceding analysis Hirth and Pound assumed: a set of parallel steps at a distance $y_0$ from each other; that the incorporation of the crystallizing atoms takes place only at the kinks; that every step has a high concentration of kinks; that consequently the steps serve as line sinks for the crystallizing atoms and the surface concentration at a step has the equilibrium value.
Hirth and Pound have carried out the mathematical analysis of their model for the case of growth from the vapor. They used the characteristic length $\lambda_s$ (already introduced in Section 3.5.2), which represents the average distance that an adsorbed atom moves on the surface before it desorbs (Equation 3-28). Then all the atoms condensing from the vapor in a strip of width $\lambda_s$ at both sides of the step diffuse towards the step and they are incorporated into it. Using the Langmuir expression for the number of atoms condensed per unit area and per unit time:

$$j = \frac{a_i (p-p_0)}{(2\pi m k T)^{1/2}}$$  \hspace{1cm} (3-37)

and assuming $a_i$, the accommodation coefficient to be equal to one (although the treatment does not change even if this assumption is not made) the current of crystallizing atoms going into the unit length of a step can be calculated

$$j = \frac{2 \lambda_s (p-p_0)}{(2\pi m k T)^{1/2}}$$  \hspace{1cm} (3-38)

where $p_0$ = the equilibrium pressure
$p$ = the actual vapor pressure
$m$ = atomic or molecular mass
$k, T$ have the usual meaning

Since supersaturation $S$ is defined as $S = \frac{p-p_0}{p_0}$ (3-38) becomes
Consequently the velocity of a step is

\[ v_\infty = j_{a} = \frac{2 \lambda_{s} P_{0} \Omega S}{a (2\pi m k T)^{1/2}} \]  

(3-40)

where \(a\) = the height of a step

\(\Omega\) = the volume per molecule in the crystal.

To derive (3-40) it was assumed that the steps have a separation \(y_{0}\) much greater than \(\lambda_{s}\). However if the distance between steps becomes of the order of \(\lambda_{s}\) or smaller the steps compete with each other, so that the diffusion to any particular step is altered (reduced) by the diffusion to adjacent steps. Consequently the velocity of each step diminishes and turns out to be

\[ v_\infty = \frac{2 \lambda_{s} P_{0} \Omega S}{a (2\pi m k T)^{1/2}} \tanh\left(\frac{y_{0}}{2 \lambda_{s}}\right) \]  

(3-41)

The growth rate \(R\) can be now calculated since,

\[ R = \frac{v_\infty a}{y_{0}} \]  

(3-33)

The distance between steps \(y_{0}\) has been estimated as we saw in Section 3.5.1, by Frank as \(4\pi \rho_{c}\) and by Cabrera and Levine as \(19\rho_{c}\). Since \(\rho_{c}\) is inversely proportional to supersaturation \(S\) (see Equation 3-32) \(y_{0}\) is also inversely proportional to \(S\). Therefore the crystal growth rate becomes proportional
to square of the supersaturation in case the Hirth and Pound model is applied. Frank's model predicted a square dependence for "low" (<0.1-1.0% probably) supersaturations, but linear dependence for higher supersaturations.

It should be emphasized, that the preceding analysis was carried out for growth from the vapor only. It could be argued, however, that a similar expression may be developed for growth from solution. In that expression the parameters would be somewhat different but the dependence of the rate on the supersaturation would be the same: proportional to square of the supersaturation.

3.5.6 Evaluation of Dislocation Theory of Growth - Comparison with Experiments

Dislocation theory of growth succeeds exactly where the two-dimensional nucleation theory failed: it predicts the right order of magnitude for the growth rate from vapor, especially at supersaturations smaller than 20-50 per cent. Both models, i.e., Frank's and that based on surface diffusion give realistic values for the resistance to growth. Frank's treatment, however, by predicting the growth rate to have a first power relationship to the supersaturation is in agreement with the results of most growth experiments. The surface diffusion resistance model, on the other hand, fails in this respect, by predicting a second power dependence. However, it explains the finite resistance to crystal growth, observed in cases where the
bulk diffusion is of no importance. In general, there are not many instances where the quantitative aspects of the dislocation growth theory have been confirmed experimentally. The few reported cases (70,112,115,163,174) in which the growth data could be correlated according to one of the above relations (3-35, 3-36, 3-41) are almost all from vapor growth. However, spiral growth traces were observed on a wide variety of crystals (168). In the growth of CdI₂ platelets from an aqueous solution, the screw dislocation growth mechanism was observed in operation (68,135). In summary then, it may be stated that a dislocation mechanism of growth is important in many cases and even may be involved to some extent in all crystal growth phenomena. The importance of dislocations in the crystal growth process has been endorsed by most workers in the field.

The failure of the dislocation growth models to account quantitatively for the growth data obtained by the various investigators may be attributed to the presence of impurities, which are present even in the most pure solutions. The primary reason, however, appears to be that the assumptions made during the foregoing treatments are questionable. Namely, it was assumed, in both treatments, that the distance between steps $y_0$ is dictated only by the curvature at the center of the spiral. This curvature is fixed by the supersaturation through
Equation (3-32). The over-all supersaturation, however, has been used by all investigators instead of the actual supersaturation at the steps at the dislocation center. It should be emphasized that the supersaturation at the surface is smaller than the supersaturation in the bulk of the solution, due to the presence of a diffusional layer of some thickness (even when bulk diffusion is not the controlling resistance). Thus, using the bulk supersaturation the smallest possible value of \( y_0 \) has been obtained. The resulting expressions (3-35), (3-36), (3-41) should be, therefore, viewed only as an upper limit upon the growth rate.

During the derivation of the above mentioned expressions an additional assumption was made; it was assumed that the spacing between steps \( y_0 \) remains constant over the crystal surface. An observation, however, of a growing surface reveals that the steps which flow on the surface are macroscopic (more than 1000 layers thick) and seldom uniformly spaced. This observation leads to the conclusion that monomolecular growth steps coalesce, for some reason, into bunches of macroscopic growth steps and the assumed constant step spacing would no longer prevail. This is probably one of the reasons the foregoing treatments of dislocation growth fail to explain quantitatively the observed growth rates.

The phenomenon of macroscopic growth steps led many investigators to concentrate their attention on collec-
tive effects, (for example bunching of steps) that accompany step movement rather than on the shapes and velocities of individual steps. This resulted in the development of the kinematic theory of crystal growth.

3.6 Kinematic Theory of Crystal Growth

The kinematic theory of crystal growth was first considered independently by Frank (73) and Cabrera and Vermilyea (47). The approach which the theory is utilizing is purely phenomenological: without considering the origin and the molecular configuration of the steps the above mentioned investigators studied the "flow" of steps moving over the surface of a growing crystal. The theory attempts to explain the morphological characteristics of the crystal - i.e. the formation of steps of greater height than the monomolecular ones, the formation of peculiar crystal forms and the establishment of the final steady state shape of a crystal - by treating only the interaction of the monomolecular steps with each other. The methods are those applied by Lighthill and Whitham (116) to problems of road traffic and river flood, in which the flow (cars, or gallons per unit time) may often be assumed to depend only on the linear density (cars, or gallons per unit length). Likewise it could be assumed that in crystals the flow of steps (number of steps passing a point on the crystal surface per unit time) depends on the linear step density (number of steps per
unit length). The following discussion will follow the treatment by Frank (73). The same treatment is equally applicable to growth as well as to dissolution of crystals. The theory, for the sake of simplicity will be discussed in two dimensions.

In Figure 3-10 a growing stepped crystal face is presented.

Let us represent with

- \( a \) the height of a step
- \( k \) the density of steps (i.e. the number of steps per unit length in the neighborhood of a particular point.) It depends in general on both \( x \) and \( t \)

\[
k = k(x,t)
\]
the flux of steps (i.e. number of steps passing that point in unit time).

linear distance in the direction of step propagation.

time.

Then

surface slope \( \frac{\partial y}{\partial x} = \frac{a}{1/k} = ak \)  

(3-43)

and velocity of an individual step

\[
v = \frac{\text{distance}}{\text{time}} = \frac{1/k}{1/q} = \frac{q}{k}
\]

(3-44)

The primary postulate of the theory is that the velocity of a step is related only to the local density of the steps, i.e.

\[ q = q(k) \]

(3-45)

From the condition that the steps must be preserved the continuity equation is obtained.

\[
\frac{\partial q}{\partial x} + \frac{\partial q}{\partial t} = 0
\]

(3-46)

because of (3-45)

\[
\frac{\partial q}{\partial x} = \frac{dq}{dk} \frac{\partial k}{\partial x}
\]

(3-47)

Substituting in (3-46), one obtains

\[
\frac{dq}{dk} \frac{\partial k}{\partial x} + \frac{\partial k}{\partial t} = 0
\]

(3-48)
Comparison of the total derivative of (3-42):

\[
\frac{dk}{dt} = \frac{\partial k}{\partial t} + \frac{\partial k}{\partial x} \frac{\partial x}{\partial t}
\]  

(3-49)

with (3-48) shows that \( \frac{dk}{dt} = 0 \) when

\[
\frac{dq}{dk} = \frac{\partial x}{\partial t}
\]

Under this condition \( k \) is constant and because of (3-45) \( q \) is a constant also. In other words in the \((x,t)\) plane \( k \) is constant for values of \( x \) and \( t \) lying on a line of slope

\[
C = \frac{1}{\frac{\partial x}{\partial t}} = \frac{1}{\frac{dq}{dk}}
\]  

(3-50)

Such a line is called a "characteristic".

Since the crystal surface slope is equal to \( ak \) (Eq. 3-43) the crystal surface slope remains constant along the "characteristic". Due to this property "characteristics" have been employed in the study of observed changes in the surface configuration during growth. One example is the question of the origin of macroscopic growth steps. Such a step may result, according to the kinematic theory, as follows:
FIGURE 3-11
FORMATION OF A STEP BUNCH
At initial time $t_0$, let the step density distribution have the form depicted in Figure 3-11b, that is a perturbation in the step density is introduced in the region included by $x_1$ and $x_2$, as a result, for example, of an increase in the strength of a screw dislocation that served as the source of the step sequence. (The increased strength can result from a random rise of supersaturation as well as for other reasons).

The characteristics with slopes $dq/dk$ are drawn from each point of the $x$ axis. (Figure 3-11a) The lines from the points left to $x_1$ and right to $x_2$ have all the same slope since $k$ is the same. However, in the region from $x_1$ to $x_2$, the characteristic have a different slope due to the increase in $k$. It is assumed that $\frac{d^2q}{dn^2} < 0$, i.e. the flux of steps decreases as the distance between steps decreases, (which is the case when diffusion fields of nearby steps interact). Therefore, the characteristics for high values of $k$, like in region $x_1x_2$ have higher slope than those for the lower values of $k$. From point $A$ the characteristic $AB$ is drawn, which has the highest slope and corresponds to the maximum $k$. The characteristics to the left and to the right of $A$ have smaller slopes. Hence, at the leading edge of the bunch, i.e. to the right of $AB$, the characteristics diverge; at the trailing edge, however, i.e. to the left of $AB$ they converge, and ultimately they meet at time $t_1$ and at the point $B$.
which is the point where the characteristic AB meets the characteristic starting at $x_1$. The change in the step density distribution in the perturbed region is represented by the change in the form of curve CD in Figure 3-lla. At time $t_1$ all the intervening step density values to the left of AB vanish and a discontinuity of density develops (Figure 3-llb), forming a "shock wave" of steps which is mathematically analogous to the shock wave in aerodynamics.

The effect of the formation of the "shock wave" of steps on the surface profile is shown in Figure 3-llc; the discontinuity in $k$ results in a discontinuity in the slope in the crystal surface, since slope is equal to $ak$ (3-43). This discontinuity in surface slope is presumably what appears as a large multilayer step during the microscopic observations of growing crystal faces.

The kinematic theory has also been applied to other problems, for example the profile of etch pits, the case of dissolution from crystal edges and the initiation of a whisker. However, it is not always very successful, and it can be said that it is still in a preliminary state. Nevertheless the kinematic theory succeeds in giving, through its phenomenological approach, a qualitative picture in some aspects of crystal growth. The formation of a large step is one case. Another case -- the interaction of step movement rates and impurity adsorption rates -- will be discussed in Chapter 4 which will be devoted to crystal growth in the presence of additives.
CHAPTER 4

GROWTH OF CRYSTALS IN PRESENCE OF ADDITIVES

Crystal growth from solutions containing other solutes besides the crystallizing species is a much more complex process than the growth from pure solutions. It is, however, a more important process since even the crystallization from what is considered as "pure" solution is in actuality crystallization from a solution containing impurities. Furthermore additives have been used extensively to modify crystal habit and facilitate control of the crystal growth.

There are various effects caused by the presence of impurities* in the crystallizing solution. Impurities may affect the rate of growth, the habit, the morphology, the properties, and the purity of the crystals that are formed.

The effects of impurities on the growth rate and crystal habit (which is determined only by the relative growth rates normal to the various crystal faces) on the one hand, and the incorporation of the impurities into the growing crystal on the other, are of interest to the present investigation and will be considered in the following sections.

*The terms "impurity" and "additive" will be used interchangeably in this chapter.
4.1 Effect of Additives on Growth Rate

The available experimental data will be presented first and possible interpretations will be subsequently discussed.

4.1.1 Experimental Data

There are numerous reports in the literature on the effects of impurities on growth rate. A majority of them, however, are qualitative descriptive observations of habit modifications, i.e. of the effect of impurities on the relative growth rates. Buckley has devoted a large part of his book on "Crystal Growth" (25) in presenting the observed effect of impurities on the rate and habit of crystals.

The usual observation is that impurities reduce the growth rate at a given supersaturation. Examples of this reduction have been found: in electrodeposition studies (67), where small additions of various substances cause large increases in the overvoltage required for deposition; in organic homopolar crystals, for example adipic acid where cationic and anionic surfactants have been used (8,130) and finally in ionic crystals. Significant effects on growth behavior of ionic crystals have been observed with both large organic molecules and inorganic ions. Characteristic examples are the change of the cubic habit of potassium chloride to octahedral by a series of dyes (25,76), the production of octahedra on sodium chloride by Cd\(^{++}\), Zn\(^{++}\) and Mn\(^{++}\), under conditions normally producing cubic crystals (143), and the modification of habit in
K₂SO₄ and K₂Cr₂O₄ crystals produced by S₂O₃⁻⁻ ions (29). Buckley (25) has emphasized two general observations. First, that impurities of both, organic molecules and dyes have a more pronounced effect on the rates of growth than on dissolution of a crystal and secondly that the effectiveness of the impurity decreases as the temperature and growth rate increases.

A point, emphasized by many investigators is the difference between the behavior of large organic molecules on one hand and inorganic ions on the other, used as additives for habit modification: a) The effects of large molecules are usually not specific; for instance a dye molecule may be effective in modifying the growth of many different substances and a similar effect on the growth of a crystal may be produced by several different dye molecules. In contrast the effect of inorganic ions appear to be much more specific; for instance Cd⁺⁺ considerably affects the growth rate of sodium chloride while its effect on potassium chloride is insignificant. b) Much larger additions of inorganic ions (up to 1 part in 10³ parts of crystallizing species in solution) are required compared to large organic molecules (usually 1 part in 10⁶) to alter completely the growth of a crystal. However, both foregoing statements are generalizations and needless to say exceptions have been reported. For instance it was found by Sears (152) that a mole fraction of lead chloride as low as
5 \times 10^{-6} \text{ greatly modifies growth of potassium chloride from aqueous solution.}

The value of these observations on the effect of impurities on crystal growth rates is diminished because of the following; first, most of the experiments were not conducted under constant supersaturation (which according to all growth theories is the important variable). The most often employed experimental procedure involved the cooling of a saturated solution and the observation of the nucleated and grown crystals. Therefore the effect of the impurities on the nucleation rate was superimposed on their effect on the growth rate. Impurities usually depress nucleation rates (so that new crystals will nucleate at higher supersaturation). Consequently some of the observed differences in the crystallization process could be due to differences in the level of supersaturation present when crystals are grown (a) with and (b) without impurities.

Secondly, the criterion used mostly for the effectiveness of an additive (especially when the effect of a series of additives was compared) was the modification of the crystal habit. Such an effect, however, shows only, that the additive is affecting the relative growth rates of the various faces, and indicates nothing about the magnitude of the effect on the absolute growth rate of each face. For example, when an additive is effective in making sodium chloride crystallize as octahedra under conditions
otherwise producing cubes, it can be concluded only that the additive retards the growth rate of the (111) face more than the rate of the (100) face. It is obvious that in cases where additives equally modify growth rates on all faces, no modification in the habit results and the effect of additives goes unnoticed.

Therefore, the best way to measure the true effectiveness is to measure the effect of an additive on the absolute growth rate of each face under conditions of constant supersaturation. With the exception of the data on the effect of surface active materials on the growth of adipic acid crystals, obtained by Michaels and his co-workers (8,126,130) hardly any information is available concerning the effect of additives on absolute growth rates. The need for such information, however, is great since only quantitative data on absolute growth rates can be helpful in the testing of the proposed theories of crystal growth in presence of additives.

There are a few examples of impurities increasing the growth rate at a given supersaturation. Sears (152) claimed that the rate of growth in thickness of thin plates of lithium fluoride was increased by additions of $2 \times 10^{-6}$ mole fraction of ferric fluoride. Beck (8) observed that the growth rate of the (110) face of adipic acid crystals was increased by an anionic surfactant at low concentrations (while at higher concentrations of addi-
Various mechanisms have been proposed to explain both the growth rate depression and the enhancement of the growth rate. They will be treated in the next sections.

The entire treatment will be based on the layer growth of crystals resulting from the motion of steps. Equation (3-33) indicates that the growth rate is proportional to the step velocity and inversely proportional to the distance between steps. Consequently additives may alter growth rates either a) by modifying the velocity of the steps or b) by changing the step spacing. The latter can be also expressed as "affecting the rate of formation of steps", since the more steps originate from a step source in a unit time the smaller the step spacing will be (at a constant velocity of the steps). Each effect will be discussed separately.

4.1.2 Effect of Impurities on the Rate of Formation of Steps

Two types of step sources can be distinguished a) surface nucleation on a perfect crystal surface and b) points on the crystal surface where screw dislocations, or more accurately dislocations with a Burgers vector having a component normal to the surface, terminate. The effect of impurities on the first type will be examined first.
a) Surface Nucleation on a Perfect Crystal Surface

The number \( J \) of nuclei formed per unit time and unit area (and consequently the number of steps) is given by an expression of the form (see Section 3.3.2)

\[
J = \nu e \frac{\pi \sigma^2 aV_c}{R^2 T^2 \ln(S+1)}
\]

where \( \nu \) is a frequency factor, \( \sigma \) the edge free energy and \( S \) the supersaturation. An impurity atom or molecule may adsorb either on the crystal surface or at the edge of the nucleus. By adsorbing on the surface an impurity may reduce the frequency factor \( \nu \). Obviously no significant effect is expected if a small fraction of the surface is covered. However, if a large fraction of the surface is occupied by impurities the reduction in the frequency of collision of crystallizing species on the surface will be pronounced.

Adsorption of impurities on the edge of the nucleus, on the other hand, will result in a decrease in edge energy of the lattice step.\(^{153} \) From Equation (3-14) it is evident that the rate of nuclei formation, and consequently the rate of formation of steps will be enhanced in that case. This effect was invoked by Sears in explaining the increase in the rate of growth of lithium fluoride crystals brought about by ferric fluoride.\(^{152} \)

b) Points at which Screw Dislocations Emerge

Impurities will alter the rate of formation of steps at points on the crystal surface, where screw dislocations
emerge, i.e. they will affect the spacing $y_0$ between successive steps as Equations (3-20) or (3-21) indicates. This equation shows that $y_0$ is related to the critical nucleus radius $\rho_c$ and, because of

$$\rho_c = \frac{\sigma v}{RTS}$$  \hspace{1cm} (3-32)

it is also related to the edge free energy $\sigma$. Impurities adsorbed at the edge of the lattice step lower $\sigma$; hence the critical nucleus radius $\rho_c$ is decreased and the spacing between $y_0$ also diminishes. In other words the number of steps emanating from the dislocation center will decrease. The growth rate $R$ may increase, since

$$R = \frac{av}{y_0}$$  \hspace{1cm} (3-33)

Beck explained in this way the enhancement of the growth rate on the (110) faces of adipic acid crystals caused by sodium dodecyl benzene sulfonate (SDBS). He suggested that the increase in step generation which results from lowered edge energies can be viewed mechanistically in the following way: When the curvature at the center of the dislocation is at its critical value, the addition of an adipic acid molecule is difficult because, at such a highly curved step, there is a lack of neighboring lattice molecules with which the adding molecule may interact. However, in spite of the high curvature the SDBS can be
adsorbed, thereby providing a kink at which a new row of solute molecules may be initiated. As a result, the step moves away from the dislocation more rapidly and the overall rate of step generation is increased. However, Beck observed also that this enhancing effect was true only for very low concentrations of SDBS. As the concentration increased, the enhancing effect disappeared, and, finally the rate decreased. It seems that as the adsorption of the impurity becomes extensive, the impurities block the adsorption sites for adipic acid and hinder in this way the incorporation of the adipic acid more than the step initiation is enhanced. The net result is a reduction in step flux due to the reduction in the velocity of advance of the steps. This hindrance effect of the impurities on the motion of steps will be considered next.

4.1.3 Effect of Additives on the Motion of Steps

Two mechanisms have been proposed to account for the effect of additives on the velocity of a step. Both predict a reduction in the step velocity and thereby, through the Equation (3-33), a reduction in the growth rate of a crystal face.

The first suggested by Cabrera and Vermilyea (47) concerns immobile impurities strongly adsorbed on the crystal surface. Their argument is similar to the one presented in Section 3.5.4 for the case of a pair of dislocations of opposite sign. When a step encounters a pair of adsorbed
impurities, it is forced to "filter through" them. Since, however, the step is anchored at the impurities it will acquire a curvature. As the step advances, the radius of curvature will decrease to a minimum value of $r_c / 2$ (where $r$ is the distance between the two impurities) and then it will start increasing again. Hence, the step will be stopped if $r_c / 2$ is smaller than the critical nucleus radius $\rho_c$ but it will squeeze itself through the pair of impurities if $r_c / 2 > \rho_c$. In the latter case, the velocity of the step is reduced according to the Equation (3-19)

$$v = \frac{v_\infty}{1 - \frac{\rho_c}{\rho}}$$

where $\rho$ is the radius of curvature of the step passing between the impurities $\rho_c$ the radius of curvature of the critical nucleus and $v_\infty$ the velocity of the step in the absence of impurities.

Cabrera and Vermilyea (47) assumed a two-dimensional array of impurity molecules on the surface of the crystal. If each molecule is at a distance $r$ from each other, a rough estimate of the velocity of a step results in the expression

$$v = v_\infty (1 - \frac{2\rho_c}{r})^{1/2}$$

or

$$v = v_\infty (1 - 2\rho_c d^{1/2})^{1/2}$$
where \(d\) is the density of adsorbed impurities ahead of the step.

The density \(d\) can be correlated to the impurity flux to the growing surface \(J_1\) (molecules/cm\(^2\)sec) if it is assumed that, as the step advances, the impurities adsorbed in the area covered by the step become absorbed into the crystal and do not offer a further obstacle to the advance of the following steps, through the expression

\[
d = \frac{v}{y_0} = J_1 \tag{4-3}
\]

It can be shown that Equations (4-2) and (4-3) have a solution only when \(v_\infty > \frac{14\rho_c^2}{J_1 y_0} \tag{4-4}\)

Since by Equation (3-33), \(R = \frac{av_\infty}{y_0}\), Equation (4-4) means that growth in the presence of impurities takes place only at supersaturations where the normal growth rate without impurities is

\[
R > 14\rho_c^2 J_1 \tag{4-5}
\]

Since \(R \sim S^m\) and \(\rho_c \sim S^{-1}\) (Equation 3-32)

\[
S^m > (\text{constant}) S^{-2} J_1 \Rightarrow S > (\text{constant}) \frac{1}{J_1^{2+m}} = S* \tag{4-6}
\]

In other words growth in the presence of impurities takes place only at supersaturations higher than a critical super-
saturation $S^*$ given by Equation (4-6).

The foregoing analysis is, however, an oversimplification. It was assumed a uniform impurity molecule density on the surface, while actually for a given average $J_1$ there will be fluctuations in the local density of impurity molecules. Cabrera (47) pointed out an interesting situation arising when the local density of impurities just ahead of a section of a step is larger than $(2\rho_c)^{-2}$, (i.e. the distance between impurity molecules is smaller than $2\rho_c$). In such a case that section of the step will be completely stopped. The following steps, as they advance will meet the anchored piece of step and create a local bunching as indicated in Figure (4-1).

FIGURE 4-1

BUNCHING OF STEPS BEHIND A REGION (R)
OF GREATER THAN AVERAGE IMPURITY CONTENT

After Cabrera (47)
The bunching will reach a certain height and then will over-ride the anchored piece of step. There is a possibility, according to Cabrera, that a dislocation is created in this way. This mechanism of dislocation generation is probably responsible for the high dislocation densities found in crystals grown from solution.

The situation becomes more complex if it is assumed that in most cases the concentration of impurities on the crystal surface is time dependent. To put it in another way, for the derivation of Equation (4-3) the density $d$ of the impurities on the surface was assumed to be independent of the crystal growth rate. This is true, however, only when the time required to establish an equilibrium concentration of impurities is small compared with the time that elapses between the deposition of successive layers. When the latter time is of the same order of magnitude or smaller than the first, then the concentration of impurities at a point on the crystal face does not attain the equilibrium value; it is actually an increasing function of the time elapsed since the passage of the previous step. (Frank in Ref. 73)

Thereby if a step slows down, for some reason, the impurity density on the surface ahead of it will keep increasing (until the equilibrium concentration is built up). This causes a further retardation of the step advance. (The steps moving behind the slowed step will soon overtake it forming a macroscopical step. This is another mechanism
for bunching of steps and formation of a macroscopic step. For the formation of such steps in the absence of impurities see Section 3.6). On the other hand, the faster a step advances, the less impurities it will encounter and the more the advance will be accelerated.

Another result of the time dependency of impurity concentration is that the steps are more impeded by the impurity when they are far apart, i.e. the spacing $y_0$ is large, than when they are close together.

It should be noted, therefore, that increased supersaturation results in an increased step velocity

$$V = V_{\infty} (1 - 2p_c d^{1/2})^{1/2}$$

(4-2)

not only through an increase in $V_{\infty}$ and a decrease in $p_c$, but also through a decrease in the impurity density $d$. Assuming a dislocation source of steps, Equation (3-20) indicates that as the supersaturation increases, the spacing between steps $y_0$ becomes smaller. Less time is therefore allowed for impurities to adsorb before the next step passes. Consequently the impurity density on the surface, $d$, decreases. A rather steep increase in the growth rate of a crystal is therefore predicted with increasing supersaturation from a solution containing impurities (at constant concentration of impurities in the solution).

It should be emphasized that in the above treatment the impurities were assumed to be immobile. However,
Cabrera and Vermilyea (47) also mentioned the case of mobile adsorbed impurities. They pointed out that in this case the critical value of supersaturation below which motion of steps is very slow or impossible will be less than that for immobile impurities since steps will move, even if the distance between impurities is smaller than $2\rho_c$, by pushing impurities along. At the limit of highly mobile impurities, the decrease in velocity of the steps will be very small.

Although Cabrera and Vermilyea’s treatment explains only the effects of immobile impurities and does not predict an effect of mobile impurities, (i.e. impurities which have a short lifetime on the surface), the second mechanism of impurity effects on crystal growth proposed by Sears (152,154) does not distinguish between mobile and immobile impurities. Sears proposed that the impurity atoms or molecules are adsorbed at growth steps poisoning in this way the kink sites. (It is unimportant to the mechanism whether adsorption occurs also elsewhere on a crystal surface than at steps). As it was pointed out in previous Section 3-3, it has been accepted that incorporation of crystallizing species into crystal can occur only at the kinks. The impurities, by adsorbing at the steps, poison kink sites and reduce the number of free kinks available to the crystallizing atoms. The result is a decrease in the velocity of steps. In other words, in Sears’ mechanism the velocity of a growth step and thereby the growth rate of a crystal face is controlled by the number
of free kinks on the step which are not occupied by impurities.

It was mentioned in Section 3.5.3 that there are ways to estimate the distance \( \lambda_0 \) between two kinks in a pure step. Cabrera and Coleman (44) describe one such way for growth from vapor which leads to the expression

\[
\lambda_0 = \frac{1}{2}a(e^{w/kT} + 2)
\]

(4-7)

where \( a \) = the height of a step
\( w \) = the energy required to form a kink.

For a typical value of \( w/kT \sim 2 \) (from simple considerations it appears that \( w \) is close to the one-tenth of the heat of vaporization) \( \lambda_0 \sim 4a \). Chernov (50) used the same approach to calculate the distance \( \lambda_c \) between kinks unoccupied by impurities in a poisoned step.

He considered a crystal growing from its vapor. He assumed that only the four simple molecular configurations shown in Figure 4-2 can occur. These are: (1) the sites with no kink of any kind (their fraction \( n_1 \)), (2) sites of pure kinks (half of them of positive sign and the other half, of opposite sign; their total fraction \( n_2 \)), (3) sites of poisoned kinks (their fraction \( n_3 = 2n_{3+} = 2n_{3-} \)) and (4) sites where an impurity is adsorbed at an edge of a step (their fraction \( n_4 \)). The density of kinks is now determined by the equations (44):
FIGURE 4-2

REPRESENTATION OF A (10) STEP ON A (100) FACE OF A CUBIC CRYSTAL

(The black cubes represent adsorbed impurity particles)
\[ n_1 + 2n_2^+ + 2n_3^+ + n_4 = 1 \quad (4-8) \]
\[ n_2 = 2n_1 e^{-w/kT} \quad (4-9) \]
\[ n_3 = 2n_1 P_1 (w_1 - w)/kT \quad (4-10) \]
\[ n_4 = n_1 P_1 e^{w_1^e/kT} \quad (4-11) \]

where \( w \) is the energy to form a kink
\( w_1 \) is the adsorption energy of an impurity at a kink
\( w_1^e \) is the adsorption energy of an impurity at the edge
\( P_1 \) is the partial pressure of the impurity
\( P_0 = (2\pi m v^2 / kT)^{3/2} \)
\( m \) is the mass of the impurity particle
\( v \) is its vibrational frequency in the adsorbed state

Solving the above four equations for \( n_2 \) and combining with Equation (4-7) one obtains the distance \( \lambda_c \) between free kinks:
\[ \lambda_c = \frac{a}{n_2} = \frac{a}{2} \left( e^{w/kT} + 2 \right) + \frac{a}{2P_0} \left( e^{w_1^e + w/kT} + 2e^{w_1^e/kT} \right) P_1 \quad (4-12) \]
\[ \lambda_c = \lambda_0 + \xi P_1 \quad (4-12a) \]

For typical values of \( w_1^e - w_1 + w \approx 0.5 \text{ ev} \), \( T = 300^\circ K \) and \( m = 50 \times 1.6 \times 10^{-24} \text{ g} \) one obtains \( \xi \approx 10^{-2} \text{a/mmHg} \). Since \( \lambda_0 \approx 4a \) relatively small values of \( P_1 \) are sufficient to increase substantially the distance between free kinks.
Chernov claims that similar estimates may be made for an impurity in an ideal solution. In that case one obtains for the distance between free kinks

$$\lambda_c = \lambda_0 + \xi_c C_1$$  \hspace{1cm} (4-13)

in which \(C_1\) is the impurity concentration in the solution and

$$\xi_c = \frac{a}{2\Omega \nu} \left(\frac{kT}{2\pi m}\right)^{3/2} e^{w_1/kT}$$  \hspace{1cm} (4-14)

where \(\Omega\) is the molecular volume of an impurity particle and \(a, m, \nu, w_1\) are as above. For the purpose of an estimate, let \(w_1 = 0.4\) eV (\(10\) kcal/mole), \(\nu \sim 3 \times 10^{12}\) sec and \(\Omega = 2 \times 10^{-23}\) cm\(^3\). Then \(\xi_c \sim 10^4a\), i.e. an impurity concentration about \(10^{-3}\) is sufficient for greatly increased distances between free kinks. It should be emphasized, however, that the expressions given for \(\xi\) and \(\xi_c\) are very approximate and the resulting numbers should be viewed only as indicating the theoretical possibility of the step-poisoning effect.

By assuming that only free kinks in the steps contribute to growth, Chernov used the above equation for \(\lambda_c\) to calculate step velocities and from them growth rates, for a crystal growing from vapor, in the following way.

Burton et al \((42)\) developed an expression for the velocity of a growth step (dislocation growth):

$$V_\infty = 2\sigma \lambda_S \exp(-w/kT) \tanh(y_0/2\lambda_S) C_0 (y_0/\lambda_S)$$  \hspace{1cm} (4-15)
where $\sigma$ is the supersaturation, $\lambda_s$ the mean displacement of adsorbed molecules, $\nu$ a frequency factor, $y_0$ the distance between successive steps and $C_0(\lambda_0,y_0)$ a factor, which is a function both of $y_0$ and of distance $\lambda_0$ between kinks in the steps. Under the assumptions made by Chernov, however, $C_0$ is a function of $\lambda_0$ only and it is given by the expression (Equation 21 in reference (42))

$$\frac{1}{C_0} = 1 + 2b \ln \left[ \frac{4b \lambda_s}{a \left[ 1 + (1+b^2)^{1/2} \right]^{1/2}} \right]$$ (4-16)

where

$$b = \frac{\lambda_0}{2\pi \lambda_s}$$ (4-17)

According to the estimates made in Section 3.5.2 and 3.5.3, in most of the cases of pure surfaces growing from vapor $\lambda_s >> \lambda_0$ (i.e. $\lambda_0 \sim 4a$ and $\lambda_s \sim 10^2 a$) and hence $C_0$ is of the order of 1. In case, however, of steps poisoned by impurities the distance $\lambda_c$ between free kinks can be very large and even larger than $\lambda_s$. Then $C_0$ is given by the Equation (4-16) in which $\lambda_0$ is substituted by $\lambda_c$. Since $\lambda_c$ is a function of impurity concentration see Equation (4-12), the dependence of the step velocity on the impurity concentration enters into Equation (4-16) and thereby into Equation (4-15) through the factor $b$ [Equation (4-17)]. The relative decrease in step velocity caused by the impurity is easily found to be
\[
\frac{V^1}{V_\infty} = \frac{C_0(\lambda_c^*)}{C_0(\lambda_o^*)} = \frac{C_0(\lambda_c)}{1} = \frac{1}{1 + \frac{\lambda_c - 1}{\pi \lambda_s} \ln \left[ 1 + \frac{\lambda_c^2}{2\pi \lambda_s} \right]^{1/2}}
\]

or

\[
\frac{V^1}{V_\infty} = \frac{1}{1 + \frac{\lambda_o + \xi P_1}{\pi \lambda_s} \ln \left[ 1 + \frac{\lambda_o^2 + \xi P_1}{2\pi \lambda_s} \right]^{1/2}}
\]

where

\[
\begin{align*}
V^1_\infty & = \text{the step velocity in the presence of the impurity} \\
a & = \text{height of the step} \\
\lambda_s & = \text{mean displacement of adsorbed molecules} \\
P_1 & = \text{partial pressure of impurity} \\
\xi & = \text{a factor given by expression (4-12)}
\end{align*}
\]

The above expression predicts that the relative rate reduction is independent of supersaturation, which is contrary to experimental observations. It seems that it would be more correct if instead of Equation (4-16), used by Chernov, the following expression giving \( C_o \) as a function both of \( y_o \) and \( \lambda_o \) had been used: (Equation 25 in reference (42)).

\[
\frac{1}{C_o} = 1 + 2b \tanh \frac{y_o}{\lambda_s} \left[ \ln \frac{4b \lambda_s}{a [1+(1+b^2)^{1/2}]} + \frac{2\lambda_s \tan^{-1} b}{y_o} \right]
\]
\[
\frac{b}{2\pi \lambda_s} = \frac{\lambda}{\lambda_0}
\]
where \( \lambda = \lambda_0 \) for a pure step
\( \lambda = \lambda_c \) for a poisoned step

Then

\[
\frac{V^1}{V_\infty} = \frac{C_o(y_o^1, \lambda_c)}{C_o(y_o^1, \lambda_0)} = \frac{C_o(y_o^1, \lambda_c)}{1} = C_o(y_o^1, \lambda_c) = C(y_o^1, p_1)
\] (4-21)

where \( y_o^1 \) is the spacing between steps in the presence of the impurity.

Then

\[
\frac{V^1}{V_\infty} = \frac{1}{1 + \frac{\lambda_o + \epsilon p_1}{\pi \lambda_s} \tanh(y_o/\lambda_s)} \left[ \ln \left( 1 + \left( \frac{\lambda_o + \epsilon p_1}{2\pi \lambda_s} \right)^{2/3} \right) \right] + \frac{2\lambda_s \tan^{-1} \left( \frac{\lambda_o + \epsilon p_1}{2\pi \lambda_s} \right)}{y_o} \right]
\] (4-22)

The growth rate normal to a crystal face can be calculated through the expression

\[
R = \frac{V_\infty a}{y_o}
\] (3-33)

Therefore

\[
\frac{R_1}{R_o} = \left( \frac{V^1}{V_\infty} \right) \frac{y_o}{y_o^1} = f(p_1, y_o^1, y_o)
\] (4-23)

Since \( y_o = 4\pi \rho_c = \frac{4\pi \rho \sigma V_\infty}{RTS} \) (3-32)
\[ \frac{R_1}{R_0} = f(p_1, \sigma, \sigma_1, S, T) \] (4-24)

Where \( R_0 \) = the growth rate for a pure face
\( R_1 \) = the growth rate for the same face in the presence of impurity
\( \sigma \) = the edge free energy for a pure step
and \( \sigma_1 \) = the edge free energy for a poisoned step.

There is no known way to estimate \( \sigma_1 \). Chernov assumed \( \sigma_1 = \sigma \) and plotted calculated values of the ratio \( R_1/R_0 \) vs supersaturation for various impurity partial pressures \( p_1 \) and for a given \( \lambda_s \) and temperature. As he pointed out, however, there are no experimental results suitable for testing the form of the curves he calculated.

Sears (153) suggested that the retarding effect of lead chloride impurity on the growth of potassium chloride crystals may be explained by his mechanism, i.e. adsorption of a complex lead ion at the growth steps and reduction, thus, of the sites available for the incorporation of the crystallizing particles.

An important consequence of the slowing-down of the crystallizing particle attachment by the Sears-Chernov mechanism is that under those conditions the concentration of solute in the neighborhood of the step is no longer maintained equal to the equilibrium value because the rate of exchange with the crystal is not fast enough. It could be argued that at the limit of very slow exchange the surface
diffusion gradient is eliminated, the surface concentration at the step equals the average concentration, and the attachment at the step becomes rate controlling. In other words the step is not a line sink for the solute particles as it was assumed in crystal growth in the absence of impurities. That means that the velocity of a step $V_\infty$ is independent of the distance between steps $y_0$, since the steps are not competing anymore for solute atoms among themselves. Hence, the growth rate normal to a crystal face is:

$$R = \frac{V_\infty a}{y_0} \cdot \frac{1}{y_0}$$

(4-25)

In other words the more steps there are on the crystal surface (small $y_0$) the larger the growth rate $R$ is. This is easily understood since the growth rate now depends upon the free "step edge surface" which is available to the solute particles. The larger the number of steps the more the free "step edge surface". High energy radiation may increase, in certain cases discussed in Chapter 5, the number of steps on a crystal surface. Under the conditions discussed above this would increase the growth rate of that crystal surface.

In conclusion, two mechanisms have been proposed for the reduction of the velocity of a step by impurities; the first (Cabrera and Vermilyea) suggests that the impurity is strongly adsorbed on the plane regions between steps and reduces the velocity by forcing the steps to pass through
them; the second (Sears-Chernov) suggests that the impurity is adsorbed on the step poisoning the active growth sites (kinks). There are no experimental evidences in favor of the one mechanism or the other.

Sears (152), however, implied that the amount of the impurity incorporated into the crystal could be used to differentiate between the two mechanisms. When the first mechanism is operating, he expects appreciable amounts of impurity to be grown into the growing crystal, while for the impurities following his mechanism, he states that "they are apparently not grown into the growing crystal in appreciable amounts".

However, it has been found (see Chapter 8) that one of the impurities, namely lead chloride, which is considered by Sears as following his mechanism (153), is captured by the growing crystal in considerable amounts. This fact, indicates that Sears' statement is not valid; actually either PbCl$_2$ is not following Sears' mechanism, or additives can be incorporated inside the crystal even when they adsorb at the kinks, or both.

In the following sections the incorporation of impurities in the growing crystals will be considered first and then the relation between the incorporation of an impurity and its effect on growth will be discussed.
4.2 Incorporation of Impurities into the Crystal

4.2.1 General

The treatment of impurity effects by Cabrera and Vermilyea (47), which was discussed in the preceding section, has assumed that impurity molecules may be incorporated into a growing crystal. Many experimental observations are available to show that such impurity incorporation actually occurs. For example, the phenomenon in analytical chemistry, known by the collective term "carrying down" is very troublesome in gravimetric analyses, causing contamination of a precipitate by undesirable impurities. In the chemical industry many compounds, when crystallized, occlude considerable amounts of impurities, making necessary a purification by repeated crystallization. Many times crystals grown in solutions containing dye molecules are colored by the dye; sometimes the dye is incorporated homogeneously into the whole crystal, but in other cases the incorporation seems to occur only on specific planes and "hour-glass" or "maltese cross" crystals result (30). Very striking examples of the incorporation of impurities in crystals are provided by radiochemists, which have been using (mainly before the introduction of ion-exchange resins) crystals of various inorganic salts as "carriers" to co-precipitate minute amounts of radioactive materials from solution. Autoradiographs showed that, as in the case of dyes, the radioisotope may be distributed either
homogeneously throughout the crystal or preferentially on certain planes.

The amount of impurity incorporated into the crystal under conditions of equilibrium, can be related to the concentration in the mother solution through the (equilibrium) distribution coefficient

\[ k_0 = \frac{C_c}{C_L} \]  

(4-26)

where \( C_c \) = the impurity concentration in the crystal

and \( C_L \) = the impurity concentration in the mother solution

Analytical chemists and radiochemists first became interested in the problem of inclusion of foreign substances in a crystal \((85,107)\) either to obtain pure precipitates or to develop crystalline systems co-crystallizing as much radioisotopes from a given solution as possible. Their interest, however, was confined in the determination of the distribution coefficients for various systems and in deriving empirical rules which would permit certain predictions regarding the co-crystallization of the particular system crystal-impurity. At the time these rules were formulated, (the first as early as 1913), the mechanism of crystal growth was not fully understood. Therefore those investigators made no attempt to correlate their finding with a mechanism of crystal growth. Their approach was simply phenomenological and rather descriptive.
Recently, however, the interest in the phenomenon of the incorporation of impurities in crystal was revitalized, due to the need for the production of extremely pure crystals. It is well known, now, that many physical properties of crystals depend on the presence of foreign atoms. Crystals, therefore, used in the study of these impurity sensitive properties (for instance optical and electrical properties as well as the effect of radiation on a crystal) should contain either no such impurities at all or a controlled amount of them. The investigators now coping with the problem of impurity occlusion are the same investigators who are studying the mechanism of crystal growth. This led to theories in which the incorporation of impurities is related to the elementary growth processes and more specifically to the concept of layer growth of crystals. These theories will be discussed after the early theories are outlined in the next section.

4.2.2 Early Theories - Phenomenological Approach

The first rule, which would permit certain predictions regarding the co-precipitation of various ions was formulated in 1913 by Fajans (66). His "Precipitation Rule" states that: "An additive cation is more strongly carried down by a crystalline precipitate the less soluble is the compound it forms with the anion of the precipitate." Hahn (85) cites examples from the precipitation of radio-
active isotopes by crystals, in which this rule applies. For example the, bismuth isotopes are carried down with barium carbonate and with iron hydroxide, but they do not separate out of acid solutions with barium sulphate. The reason given is that bismuth carbonate and bismuth hydroxide are of very low solubility, while bismuth sulfate dissolves readily in acid solutions.

Fajans precipitation rule proved very helpful to the radiochemists at the time it was formulated. Later, however, numerous observations were accumulated, that could not be reconciled with that simple rule. For example, the lead isotope, thorium B, is not brought down with a precipitate of mercuric iodide or mercurous iodide, although lead iodide is only very slightly soluble.

These discrepancies led Hahn to the conclusion, that low solubility alone, in the sense of the Fajans rule, could not be the sole condition determining the co-precipitation of these extremely small amounts of impurities (85).

Hahn shifted the attention from the solution to the crystal itself and looked at the factors which affect the accommodation of the impurity atoms inside the host crystal lattice. First, he drew up a systematic classification of the processes underlying the co-precipitation of the small amounts of impurity by a growing crystal. Three different groups may be distinguished.
I. Precipitation or incorporation processes in which a true isomorphism exists between the impurity and the host crystal. Impurity and crystallizing species can form mixed crystals. In this case the growing crystal can incorporate into its lattice an impurity particle as easily as a crystallizing particle, since it cannot "distinguish" between the two isomorphous particles. It is obvious that in this case the ratio of the two components in the crystal is determined by their ratio in the solution at the crystal surface and that precipitation could occur under all conditions.

II. Processes in which the impurity is merely adsorbed at the surface of the crystal without being incorporated inside the lattice. In this case the amount precipitated depends upon the surface-to-volume ratio of the crystals. It is obvious that formation of large, well grown crystals will decrease adsorption or merely suppress it.

III. This group includes all cases which do not fall into group I or II. In other words the processes where the impurity is included inside the crystal although the conditions of isomorphism are not fulfilled. In all these cases the formation of mixed crystals between impurity and host crystal could not have been anticipated on chemical or crystallographic grounds. The ready detection of radioactive substances at minimal concentrations enabled Hahn
to discover numerous systems in which radioactive atoms are carried down by crystals although no isomorphism was involved.

The cases of impurity incorporation, in which the present investigation is interested, belong to group III. The impurities used were selected because of their property to affect the growth rate of a crystal. An impurity which can isomorphously replace an ion in the lattice of a crystal is not expected to affect the growth rate of the crystal. Judging from the observed effect on crystal growth rate of the impurities used in the present study, it is deduced that they did not crystallize isomorphously inside the crystal.

Hahn and his co-workers conducted a series of experimental investigations using radioactive isotopes as impurities, in an effort to interpret this "anomalous" inclusion (85). Their results, correlated also with the results of other investigators were not very illuminating towards this direction, although some of the findings were very interesting (to be discussed in a subsequent section). The main reason was, that, as in the vast majority of the crystallization data, the condition of constant supersaturation (necessary for obtaining meaningful results) was overlooked. The conditions of crystallization varied from investigator to investigator. In some cases the crystals were obtained by rapidly cooling a saturated solution while
in others by slow evaporation of the saturated solution. Another source of contradictions arises from the failure to establish conditions at which the diffusional processes were not the controlling step. In most of the cases very slow stirring or no stirring at all was provided. It is not surprising, therefore, that the laws of distribution for the same system deduced by different investigations failed to agree.

Generally speaking, two different types of distributions have been distinguished.

Let $a$ and $b$ be the initial concentrations of two ions in the solution, and $x$ and $y$ the amount of each crystallized. The distribution formula (4-26) would read

$$\frac{x}{y} = D \frac{a-x}{b-y}$$ (4-27)

$D$ being the a constant, i.e. the distribution coefficient. This distribution formula implies that the whole crystal is in equilibrium with the solution, and the ratio of the two ions is the same throughout the whole crystal. It is obvious that this can be achieved only in any one of the following two cases. First, if $x$ and $y$ are very small compared with $a$ and $b$ and the concentrations in the solution could be assumed constant. Secondly, if diffusion within the crystal is very fast, as is true in the case of liquids.
If it is assumed, however, that no exchange is possible between the interior of the crystal and the solution (diffusion within the crystal negligible) then the interior is screened from the solution by the outer layers of the crystal and the distribution has the following logarithmic form

$$\ln \frac{a}{a-x} = \lambda \ln \frac{b}{b-x}$$

(4-28)

$\lambda$ being the distribution coefficient under these conditions. This law is easily deduced if we assumed that each new layer is in equilibrium with the solution. Then

$$\frac{dy}{dx} = \frac{1}{\lambda} \frac{b-y}{a-x}$$

(4-29)

and on integrating Equation (4-28) results. This equation states that if $\lambda < 1$, the concentration of an impurity is at a minimum at the beginning of the crystallization and that the crystal layers formed later will be successively richer in the impurity corresponding to the progressive increase in impurity concentration in the solution. The opposite is true if $\lambda > 1$.

Determinations of the distribution coefficients $D$ and $\lambda$ for various systems has been reported extensively in the literature. Depending on which coefficient $D$ or $\lambda$ is constant a system is characterized as following the $D$- or $\lambda$- distribution law. However, many systems have been characterized by some investigators as $D$ and by others as $\lambda$. Moreover the value of $D$ or $\lambda$ has been found to change when the conditions of crystallization change.
characteristic example is the incorporation of radium in crystals of barium salts. Doerner and Hoskins (60) and also Riehl and Kading (141) found that the distribution of radium is logarithmic but Henderson and Kracek (91) and also Chlopin and others (51) observed a homogeneous distribution. Moreover, Riehl and Kading found that \( \lambda \) becomes smaller the faster the rate of crystallization. Hahn and his co-workers showed that it is possible to select the experimental conditions so that at one time the logarithmic and at another time the homogeneous distribution of the radium could be secured. Roughly, logarithmic distribution is associated with slow, and homogeneous distribution with fast crystallization. No satisfactory explanation was given for the homogeneous distribution of Ra. Hahn stated (85) that, "the facts available at present do not permit a definite answer to this question [why Ra is distributed homogeneously]." However, he suggested that the probable reason for the observed variations in the nature of the distribution and in the value of coefficients* is that the distribution equilibrium between the top layers of the crystal and the solution is hardly attained when a crystal grows very fast. Under such circumstances the time interval between the deposition of two successive layers is too

*One reason for the variation is of course the fact that theory predicts a constant relation between activities, and activities as a rule vary with the concentration. For a low concentration of impurity however, this effect will be small and may be neglected.
short for equilibrium to be achieved. Hahn's suggestion can explain why in a crystal concentrations of impurity smaller than those expected from the equilibrium distribution coefficient may be found. It fails however to explain why in some crystals impurity is incorporated in larger amounts than an equilibrium concentration. Nevertheless, Hahn's suggestion is very significant since for the first time the idea was put forward that the amount of impurity in a crystal is determined by the kinetics and not the thermodynamics of the particular growth situation. Therefore a complete knowledge of the process of impurity incorporation is possible only when the kinetics of crystal growth are understood.

4.2.3 Recent Theories - Consideration of Elementary Processes of Growth

Since it was realized that a knowledge of the equilibrium concentration of an impurity in the crystal is not necessarily helpful in predicting how much impurity would be captured by the growing crystal, investigators started probing the mechanism through which kinetic factors affect the incorporation of the impurities. If one knows the dependance of the apparent distribution coefficient on the conditions of crystal growth (i.e. rate of growth, stirring rate etc.), then he can select the conditions at which the crystal incorporates a pre-determined concentration of impurities. This is particularly important in the growth
of semiconducting crystals from melt, where the introduction of controlled concentrations of impurities is very desirable. For this reason, the first theories proposed to account for the non-equilibrium capture of impurities were in the field of crystal growth from melt. One of the most successful theories (which could be extended to apply in growth from solution) is that proposed by Hall (86). According to this theory the number of impurity atoms incorporated into the crystal is determined by the adsorption of impurities at the liquid-solid interface. In other words the impurity atoms adsorbed at the interface, are built into the growing crystal, thus giving rise to a distribution which at fast rates of growth corresponds to a distribution coefficient $k_g$ - which characterizes the concentration of adsorbed impurity atoms in the surface layer relative to that in the liquid - rather than to the equilibrium between the bulk of the crystal and the liquid. The distribution coefficient $k_g$ is generally larger than the equilibrium distribution coefficient between the bulk of the crystal and the liquid $k_0$. Thus, after each surface layer is covered and becomes an interior layer its impurity concentration is higher than in equilibrium; its composition will then tend to approach equilibrium and diffusion of the impurity atoms towards the interface will begin. If new layers are added too rapidly, however, the impurity atoms have insufficient time to exchange with
the surface and material of non-equilibrium concentrations will grow. Hall's mechanism leads to a variation of the distribution coefficient, $k_{\text{eff}}$, with crystal growth rate, $R$. The expression arrived at for $k_{\text{eff}}$ is:

$$k_{\text{eff}} = k_0 + (k_s - k_0)\exp(-\frac{R_1}{R})$$

(4-30)

where $k_0$ = equilibrium distribution coefficient between the bulk of the crystal and the liquid

$k_s$ = distribution coefficient between the surface and the liquid

$R$ = the crystal growth rate, and $R_1$ = "the growth rate for which the time interval between the deposition of successive layers to the crystal is equal to the relaxation time for the change in impurity content of a layer which has just been covered." According to this expression, $k_{\text{eff}} = k_0$ when $R_1 >> R$; and $k_{\text{eff}} = k_s$ when $R >> R_1$.

The variation of $k_{\text{eff}}$ with $R$ is shown schematically in Figure (4-3) for a case with $k_s > 1 > k_0$.

Such a case appears to be the incorporation of certain
impurities in germanium and silicon. Weiser(177) has calculated theoretically the impurity distribution coefficients in germanium and silicon. He found them to be smaller than one. In practice, however, crystals of germanium can be grown with impurity distribution coefficient higher than one.(10,86) Such a phenomenon can be explained by an adsorption mechanism.

By the way of illustration Hall himself cites the following example: using the measured values for diffusion of Sb in Ge, extrapolated to the melting point he finds $D = 5 \times 10^{-10} \text{cm}^2/\text{sec}$. The relaxation time for Sb in Ge could be, then, estimated by calculating the time $t$ required for diffusion through a distance of one atomic layer of Ge ($6 \times 10^{-8} \text{cm}$):

$$t = \frac{(\text{distance})^2}{D} \approx 7 \times 10^{-6} \text{ sec}$$

This deposition time corresponds to a growth rate $R_1$ of about 31 cm/hr. It is significant, as Hall noted, that this is close to the range of Ge growth rate values where pronounced variations in Sb concentrations are observed.

Hall's theory has received fresh support by the investigation of Bennet and Longini (10). They found that under conditions of extremely rapid growth (dendritic growth) $k_{\text{eff}}$ for In and Al in germanium is 5 and 2, respectively, whereas the quasi-equilibrium value at low growth rates is $10^{-3}$ and $10^{-1}$. 
Equation (4-30) was derived by Hall on the assumption that the crystal grows continuously. This assumption seems to be valid for the growth from melt. There, the surface, having a temperature close to the melting point, is a "diffuse interface", which means that the transition region increases from one to several molecular layers (44). In the case for growth from vapor or solution, it is assumed that the crystal grows stepwise by the successive addition of layers of a certain thickness. Chernov has given a theoretical treatment of the Hall model on this basis, assuming the addition at a fixed frequency of layers of a certain thickness (49, 50).

Chernov pointed out, that the equilibrium concentration of an impurity in a crystal can be characterized, not by one, but by three quantities: the concentration \( C_c^0 \) in the bulk crystal, \( C_s^0 \) in the surface layer (position 1, in Figure 4-4) and \( C_e^0 \) in steps (position 2, in Fig. 4-4).

**FIGURE 4-4**

VARIOUS POSITIONS FOR IMPURITY ATOMS

1. In Surface - 2. In a Step
These quantities are determined by the heats of solution and entropies of the three-, two- and one-dimensional solid solutions. Chernov (42) indicated that they can differ considerably from each other, and in some cases by orders of magnitude.

Different relaxation times are required to establish equilibrium in the three cases; the three-dimensional solution has the longest and the one-dimensional the shortest. If the crystal grows very slowly, an equilibrium impurity concentration exists in all three cases. As the growth rate increases, however, the concentration in the bulk of the crystal deviates from the equilibrium value first, followed later by the other two. The case will be assumed in which the growth rate is such that the outermost layer of the crystal is in equilibrium. When new steps are deposited on the crystal (as a result of advancing steps) this surface layer becomes part of the crystal bulk, in which case its impurity concentration is not the equilibrium one, and diffusion sets in. If \( C_s^0 > C_c^0 \) impurity diffusion to the surface will begin. Assuming now that the crystal grows by the advancement of macroscopic layers on its surface, let the thickness of the newly deposited layer be \( h \) and the impurity diffusion coefficient in the crystal be \( D_i \); then the diffusion rate is of the order \( D_i/h \). In case \( D_i/h \) exceeds appreciably the crystal growth rate \( R \) the impurity concentration in the bulk can reach
equilibrium, but when \( \frac{D_i}{h} \ll R \), then the crystal will have a non-equilibrium impurity content.

Chernov \((50)\) determined theoretically this non-equilibrium capture (or distribution) coefficient \( k_{\text{eff}} \) as a function of the crystal growth rate, the impurity diffusion coefficient in the crystal and the thickness of the deposited macroscopic layer. He arrived at a very complicated expression, the over-all result, however, was very similar to that of Hall, \( k_{\text{eff}} \) varying monotonically from \( k_o = \frac{C_o}{C_L} \) (\( C_L \) is the impurity concentration in the liquid) at low growth rates to a value which is virtually identical with the distribution coefficient between the surface of the crystal and the solution at large growth rates. Chernov's treatment, therefore, did not materially change the result of Hall's theory.

Chernov, however, although he assumed in his treatment equilibrium between the impurities in the surface and in the solution, pointed out that the concentration of the impurity at the surface may not necessarily be equal always to the equilibrium value; actually it may be smaller. The reasons can be easily visualized. First the concentration at the surface could be limited by a diffusional resistance in the liquid, and secondly the growth rate could be so large that the surface is covered by a new layer before it has time to acquire the equilibrium impurity concentration.
It appears that an interrelation of the Hall-Chernov model of non-equilibrium impurity incorporation in the crystal with the Frank's model of time-dependent concentration of impurities at the crystal surface (73) (see also Section 4.1.3) is desirable. This will be attempted in Chapter 8 after the various experimental data on non-equilibrium uptake of impurities from solution are reviewed and the results of the present investigation on the same topic are presented.

4.2.4 Previous Experimental Observations on the Impurity Incorporation of Crystals from Solutions

The solubility of the impurities is generally considered (160) to be greater in the solution than in the crystal. Purification of crystals by re-crystallization is based on this phenomenon.

Chernov's treatment, however, predicted that there should be cases where a non-equilibrium capture of impurities, will result in crystals having a higher concentration of impurities that the solution i.e. the effective distribution coefficient between the bulk of the crystal and the liquid \( k_{\text{eff}} > 1 \).

In the same paper (50) although Chernov cited data supporting his model for the case of growth from melt, he implied that similar data were not available for the case of growth from solution.
A survey of literature showed, however, that such phenomena have been observed, although mainly by investigators not interested in the growth of crystals. Radiochemists have observed that a radioactive ion present at high dilution would come down as a mixed crystal when another salt was crystallized from the solution although most of the times the criteria for isomorphism were not fulfilled. In some cases the distribution coefficient, \( k_{\text{eff}} \), was larger than unity. Such cases are the following:

a) Hahn and his group of investigators have reported \( (85) \) distribution coefficients larger than one for the systems: ThB (which is actually an isotope of lead) in alkali halides of sodium chloride type lattice, ThB in SrSO\(_4\) crystals and finally ThB and ThX(Rd) in alkali sulfates (K\(_2\)SO\(_4\), Rb\(_2\)SO\(_4\), (NH\(_4\))\(_2\)SO\(_4\)).

b) Booth \( (18, 19) \) reported similar results for the systems, ThB in NaCl and cadmium in NaCl and

c) Yamamoto \( (180) \) using very high concentrations of impurities found a \( k_{\text{eff}} > 1 \) for Pb in NaCl, KCl, KBr, and RbCl.

The results of the foregoing investigations will be presented now in detail.

a) Investigations by Hahn's Group

Hahn in his book, "Applied Radiochemistry", \( (85) \) points to the following cases observed either by himself or by other radiochemists:
ThB in Alkali Halides. In the case of alkali halides which crystallize with the NaCl type of lattice (face-centered cubic), viz. NaCl, KCl, KBr a pronounced coprecipitation of Thorium B took place. The amount of ThB incorporated into these crystals was constant for a given starting impurity concentration, and was quite independent of the working conditions. The amount of ThB or Pb added to the solution varied from practically weightless quantities of Thorium B (1 x 10^{-10} gm per mol of the salt) up to several mol per cent. The values of the constant distribution coefficient D (as defined in Section 4.2.2) for low ThB concentrations, (not specified) are summarized in Table 4-1. In the same table the coefficient D for halides crystallizing in the cesium chloride lattice (body-centered cubic) is presented. It is evident that Thorium B (lead) is highly concentrated in the sodium chloride type lattice but not in the cesium chloride lattice.

**Table 4-1**

<table>
<thead>
<tr>
<th>Sodium Chloride Type</th>
<th>CsCl Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt</td>
<td>D</td>
</tr>
<tr>
<td>NaCl</td>
<td>60</td>
</tr>
<tr>
<td>KCl</td>
<td>57</td>
</tr>
<tr>
<td>KBr</td>
<td>60</td>
</tr>
<tr>
<td>NaBr</td>
<td>25</td>
</tr>
</tbody>
</table>

*Crystallized at -200°C*
To support further the idea that the type of lattice determines whether or not lead will be incorporated into the crystallizing precipitate, Hahn determined the amount of lead in monoclinic hydrated sodium chloride and sodium bromide, which can be obtained at very low temperatures. In both cases D was determined to be less than 0.1, so the amount of precipitated lead is negligibly small.

ThB in SrSO₄. When strontium sulphate is precipitated in the presence of Thorium B, about 99 per cent of the impurity is found in the crystal, even if only 50 per cent of the strontium sulphate is brought down. If, however, an alkali halide is added to the solution before the sulphates are precipitated, the amount of lead in the crystal decreases steadily with increasing halide concentration.

Hahn interpreted this as meaning that the lead ions, in the presence of the alkali halide, are converted into a complex state, possibly \( \text{[PbCl}_4\text{K}^- \). These negatively charged alkali lead halide ions cannot be captured by strontium sulphate. However, they can be co-precipitated during the crystallization of alkali halides.

ThB, ThX and Po in Alkali Sulphates. Radioactive ions were also found to be incorporated considerably in various sulphate salts. The salts, studied by Hahn, were anhydrous sulphates of potassium, rubidium and ammonium. The radioactive types employed were ThB(Pb), ThX(Ra) and polonium.
The distribution coefficients were found to be larger than 1 in the case of Pb and Ra but not in the case of polonium. In contrast, however, to the case of alkali halides and lead where the distribution coefficient $D$ was remarkably constant, in the case of the alkali sulphates $D$ was not constant. In the co-precipitation of potassium or rubidium sulphates with lead or radium, the observed distribution coefficients usually varied between 15 and 30, but much higher values and even lower ones were sometimes determined. For ammonium sulphate $D$ varied between 2 and 4.

This difference led Hahn to assume two types of non-isomorphous (i.e. of group III, described above) inclusions of an impurity inside a crystal: the "anomalous mixed crystals" represented by the case of ThB in alkali halides and the "internal adsorption compounds" represented by the incorporation of ThB and ThX in alkali sulphates. In the first type the radioactive ion is distributed throughout the whole mass of the crystal lattice, while in the second the impurity is distributed unevenly on the different planes of the crystal. Thus, besides the criterion of the constancy of $D$, two other criteria were introduced by Hahn in order to distinguish between the two types: a) In "anomalous mixed crystals" the impurities should be homogeneously distributed in the host crystal and b) the distribution coefficient $D$ should not be affected by an other adsorbable impurity present in the solution in the case of "the
anomalous mixed crystals". In the "internal adsorption compounds", however, the impurity is incorporated into the crystal by adsorbing on crystal planes developed during the growth. Therefore, other ions which can adsorb on the same plane may displace the original impurity ions and reduce their distribution coefficient.

Hahn obtained autoradiographs* which showed that Ra is not homogeneously distributed in a potassium sulphate crystal but it is deposited in different amounts on different planes. This classifies the above system as an "internal adsorption compound".

On the other hand, Hahn was unable to find ions which could reduce the uptake of ThB by alkali halides, thus justifying his classification of this system as "anomalous mixed crystal". However, Booth in 1938, found such an ion which can replace ThB in an alkali halide lattice.

b) Investigation by Booth

Uptake of ThB by NaCl. Booth observed (19) that the inclusion of ThB in NaCl can be prevented by the presence of an excess of cadmium ions. From this and other observations, he concluded that the distinction between the two classes of non-isomorphous

*An autoradiograph is obtained if a crystal face containing a radioisotope, is placed against a photographic plate in the dark; the subsequently developed plate will show the distribution of the radiating impurity, by appearing dark in the places corresponding to high impurity concentration.
co-crystallization is of doubtful value. In all cases, according to Booth, an adsorption of the foreign ions on specific crystal planes is involved. Whether an impurity will be distributed in the whole crystal or not, depends entirely on whether crystallographic planes on which the impurity does not adsorb appear during the growth process. Figure 4-5 for instance represents a section of a cubic crystal cut parallel to an (100) face. It is assumed that the crystal has only developed (100) and (110) faces.

![Diagram of crystal faces](image)

**FIGURE 4-5**

**INHOMOGENEOUS INCORPORATION OF IMPURITIES IN A CRYSTAL**

(Crystal section cut parallel to an (100) face)
and that an impurity can be adsorbed on an (100) face but not on an (110) one. Then the crystal will contain impurity only in the sections represented by the dark areas in the Figure. If the impurity is radioactive, Figure 4-5 would resemble an autoradiograph.

Uptake of Other Ions by NaCl. Booth, further, investigated the uptake by the NaCl crystals of cadmium, zinc, manganous, mercuric and bismuth ions. He used radioactive isotopes of these ions at concentrations about 0.1 µg per ml of solution. He found that only cadmium was captured by NaCl in the same way as Pb. The cadmium distribution coefficient, estimated as D, (see Equation 4-27) was found to be roughly constant. Its value was about 20, somewhat less than for lead, which was found to be 60, also by Booth.

An upper limit for the incorporation of Pb and Cd in the NaCl crystal was found, which corresponded to 0.006 mole per cent. The existence of an upper limit indicates that as the concentration of the impurity in the solution increases, after a certain point the distribution coefficient will decrease, since the fraction of the impurity precipitated will become smaller.

Autoradiographs of ThB in NaCl. Booth also obtained autoradiographs of ThB in a NaCl crystal. Contrary to Hahn's autoradiographs which showed an approximately homogeneous distribution of ThB through the whole crystal, Booth's showed that the ThB concentrated to a greater extent on the 100 faces than on
the (111) faces which were also present in the crystal. Neither investigation, however, gives a conclusive answer to the question, whether ThB (or Pb) is adsorbed only on (100) faces or on (111) faces as well. In Hahn's autoradiographs the crystals, which showed homogeneous distribution of ThB, had developed (100) faces only, for the amount of ThB in solution was too small to cause habit modification and development of (111) faces. On the other hand, Booth, in order to develop (111) faces used Bi ions in the solution, and the possibility cannot be ruled out that competitive adsorption of Bi on (111) planes is the cause for the non-adsorption of lead.

Uptake of ThB by LiCl. The possibility that the structural type of the crystal is the controlling factor was ruled out by Booth. In contrast to Hahn's statement that the criterion for the incorporation of ThB in an alkali halide crystal is whether its lattice is face-centered or not, Booth observed that the amount of ThB taken up by the face-centered LiCl is nearly zero.

c) Investigation by Yamamoto

Yamamoto also studied the uptake of impurities by alkali halides. He did not use radioisotopes and had to rely on conventional analytical methods. For that reason, he employed high concentrations of impurity, in some cases as high as an 8 mole per cent in the solution. (180) His results for the effective distribution coefficient of the
impurities which he tested are summarized in Table 4-2.

**Table 4-2**

Effective Distribution Coefficients of Various Impurities in Alkali Halide Crystals

<table>
<thead>
<tr>
<th>Salt</th>
<th>1-20</th>
<th>l</th>
<th>0.01-0.1</th>
<th>0.002-0.004</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>Pb</td>
<td></td>
<td>Mn, Bi</td>
<td>Cr, Ni</td>
</tr>
<tr>
<td>KCl</td>
<td>Pb</td>
<td></td>
<td>Bi</td>
<td>Ni, Mn</td>
</tr>
<tr>
<td>KBr</td>
<td>Pb</td>
<td></td>
<td>Mn</td>
<td></td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td></td>
<td></td>
<td>Mn, Cd</td>
<td></td>
</tr>
<tr>
<td>RbCl</td>
<td>Pb</td>
<td></td>
<td>Ni*, Co, Cr</td>
<td></td>
</tr>
<tr>
<td>LiCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td></td>
<td></td>
<td></td>
<td>Pb</td>
</tr>
</tbody>
</table>

*For Ni in some cases $k_{eff}$ was as high as 1.5

In most cases Yamamoto's crystallization experiments were conducted by slowly evaporating a solution in an oven at a temperature between 45° and 50°C. Hence, his results had only qualitative value, since again the supersaturation and consequently the growth rate were not constant. In addition since the solution was not stirred, the diffusion of the impurity through the boundary layer close to the crystal surface was probably the controlling step.

In most of the cases the amount of impurity taken up increased as the concentration of the impurity in the solu-
tion increased. A characteristic example is the system Bi in KCl crystals (Figure 4-6). In two cases, however, namely Pb in KCl and NaCl, the amount of impurity in the crystal goes through a maximum (Figure 4-7).

It is expected the impurity content of a crystal would become constant, after a certain point, reaching a saturation state. It is difficult, however, to visualize why it would become smaller.

Yamamoto does not offer an explanation. An interesting observation, however, is mentioned by him; crystals grown in solutions, which contain Pb$^{++}$ in concentrations lying to the left of the maximum of the curve (Fig. 4-7) develop mainly (100) faces, but when they grow from solutions with Pb$^{++}$ concentrations lying to the right of the maximum they develop only (111) faces. This evidence, matched with the above mentioned tentative conclusion by Booth (that Pb$^{++}$ is not adsorbed on (111) planes), could give an explanation; namely that the crystals, grown from solutions with high concentration of Pb, contain less Pb, because those crystals consist mainly of (111) faces on which lead ions do not adsorb.

It should be noted, that Yamamoto was using the nitrate of lead as an additive. Thus when the concentration of lead in the solution was increasing, the concentration of nitrate anions was also increasing at the same time. It is possible that this fact is responsible for the decreas-
FIGURE 4-6
INCORPORATION OF Bi IN KCl CRYSTALS
(According to Yamamoto (180))

FIGURE 4-7
INCORPORATION OF Pb IN KCl AND KBr CRYSTALS
(According to Yamamoto (180))
ing uptake of lead at high lead concentrations in the solution.

The postulation by Booth, that adsorption is responsible for the capture of impurities or additives by crystals leads to the following two questions:

a) Why certain ions adsorb strongly on a crystal face (for instance Cd and Pb on NaCl) and are thereby incorporated into the crystal while others do not adsorb at all and are not taken up by the growing crystal?

b) Is there any correlation between the uptake of an additive by a crystal and the effect of the same additive on the growth of the crystal (which effect has been also attributed to adsorption)? In other words, are the additives which are captured by the growing crystal, the same ones which retard the growth of a crystal face by adsorbing on it?

These questions will be discussed next.

4.2.5 Mechanism of Additive Adsorption

Booth discussed in his paper (18) the "lattice-fitting" hypothesis. This hypothesis, suggested among others by Royer (143), states that for an impurity to adsorb on a crystal face, this face should have a regular repetition of atom-pattern, approximating sufficiently some plane in the impurity crystal (when crystallized) and that cations and anions in the two should be similarly arranged and at similar intervals. On this basis, Royer (143), offered an
explanation for the adsorption (as it was manifested by the habit modification) of Pb on KCl (not NaCl). He noted that if a unit rectangle is described on the (111) face of the KCl lattice it has almost the same dimensions as the (100) face of the orthorombic PbCl$_2$, i.e. only 3 per cent misfit. To extend this idea to adsorption of Pb in NaCl and LiCl there would be 11 per cent and 20 per cent misfits in the lattices, respectively. The incorporation of Pb in the halides follows the order: more Pb in KCl > NaCl > LiCl. This fact, therefore, is in conformity with the lattice-fitting hypothesis.

However, if we consider the case of PbCl$_2$, CdCl$_2$, ZnCl$_2$ and MnCl$_2$ in NaCl, the corresponding misfits are 11, 3, 5, and 7 per cent. This seems surprising in view of Booth's observation that both Pb (which presents the largest misfit) and Cd adsorb on NaCl strongly, while Zn and Mn very weakly. This, obviously, makes the lattice-fitting hypothesis considerably less plausible.

There is no reason to assume that adsorption would occur by the parallel deposition of crystal layers of impurity, as the lattice-fitting hypothesis is implying. It is more likely that adsorption is by single ions strewn about the adsorbing surface in a statistically manner. Therefore, for a complete understanding it would probably be necessary to consider the nature of the ions in the solution and the possible formation of complex
ions of the additive with the crystallizing salt either in the solution or in the crystal surface.

To sum up, the uptake of an impurity by a growing crystal is caused by the adsorption of the impurity on the faces of the crystal. The subsequent covering of the surface layer by a new layer leads to non-equilibrium impurity concentrations in the crystal. The question why some additives adsorb stronger than others still remains unanswered.

4.2.6 Recapitulation of Section 4.2

The amount of impurity incorporated into a crystal under conditions of equilibrium, can be related to the concentration in the mother solution through an equilibrium distribution coefficient \( k_0 \). Purification of crystals by recrystallization is based on the inequality \( k_0 < 1 \).

However, cases have been reported in the literature where the produced crystals have a higher concentration of impurities than the solution. These cases are: ThB(Pb) in alkali halides of the NaCl type and alkali sulphates, ThX(Rd) in alkali sulphates, and Cd in sodium chloride.

Hall introduced a theory, according to which even in the cases where \( k_0 < 1 \), a mechanism for non-equilibrium incorporation of impurities may be operating, so that crystals are produced having an effective distribution coefficient, \( k_{\text{eff}} > 1 \).
According to his theory, the number of impurity atoms incorporated into the crystal is determined by the adsorption of impurities at the liquid-solid interface. Let $k_s$ be the surface distribution coefficient and let it be assumed $k_0 < 1 < k_s$. Then, as the crystal grows, the impurity atoms, which are adsorbed at the interface are built into the growing crystal, thus giving rise to a distribution, which at fast rates of growth corresponds to the surface distribution coefficient $k_s$. At low growth rates - compared to the diffusion rate - however, the impurities have sufficient time to diffuse to the interface, and the resulting crystal has the equilibrium distribution coefficient.

Hall's theory was developed initially for crystals growing from the melt. Recent investigations in that field are supporting his postulate.

Chernov developed a similar theory applying also to crystals growing from vapor or solution. He determined theoretically that the effective distribution coefficient will vary monotonically from $k_0$ when $D_i/h \gg R$ to $k_s$ when $D_i/h \ll R$, where $D_i$ is the diffusion coefficient of the impurity coefficient in the crystal, $h$ the thickness of the deposited layer and $R$ the growth rate of the crystal.

Chernov assumed in his treatment that the adsorption of the impurity at the crystal surface attains equilibrium.
4.3 Relation Between Impurity Incorporation and Effect on Growth

The foregoing discussion on the incorporation of an impurity in a crystal on the one hand and the discussion on the effect of impurities on the growth of crystals on the other indicated that both may be attributed to adsorption.

The question, therefore, arises, whether it has been established experimentally that the impurities which retard growth are also strongly incorporated into the crystal. The answer to this question may be helpful in elucidating the mechanism of growth retardation by impurities.

Yamamoto answered the question positively (180). He used as a criterion for the effect of the additive on the growth rate, the form of the crystal; i.e. the ions which retard growth are helpful in the production of well-formed crystals. On this basis he found that the higher the impurity distribution coefficient the more effective the impurity in retarding the growth of the crystal. The ions listed in the last column of Table 4-2 do not have any effect on the growth of the corresponding crystals. At the same time their incorporation in the crystal is negligible. Actually the uptake is so small that it can be attributed to entrapped mother liquid.
Another characteristic example is the lead ion. Lead is most influential on the growth of the crystals of NaCl, KCl, KBr, and RbCl (Table 4-2) and is contained in them in considerable amount, while in the crystal of NH$_4$Cl, on whose growth it exerts no influence it is contained in a negligible amount.

Another criterion, which has been used for judging the effect of an additive on growth, is the habit modification. It has been observed that lead modifies the habit of many alkali halides of the sodium chloride type, producing the (111) face, but does not affect those of the cesium chloride type(180). At the same time, it is evident from Table 4-1 that ThB (lead) is strongly incorporated into sodium chloride-type and not cesium chloride-type lattices. Thus, the incorporation of an additive in the crystals would be correlated empirically with the habit modification effect.

However, certain observations contradicting this conclusion have been reported. Booth (18) working with NaCl found that, although it is difficult to express the habit modification effect quantitatively, the order of the effect is Bi, Cd > Pb >> Mn, Zn, Hg; that is Bi and Cd have the largest effect followed by Pb; Mn, Zn, Hg have a minimal effect and give only very small octahedral corners to the cubic forms even at the highest possible concentrations. It is true, that the incorporation of
of Mn, Zn, and Hg (see Section 4.2.4b) is very small ($k_{\text{eff}} \ll 1$) and of Pb and Cd very high ($k_{\text{eff}} > 1$). However, the distribution coefficient of Cd and Pb are in reverse position as compared with their effect on crystal habit. The chief discrepancy however is the Bi. It affects the habit of NaCl, which means that it slows down the growth rate on (111) faces and probably on (100) faces and is consequently adsorbed on these faces but it is not incorporated into the crystal to the level of detection.

There are other examples showing also that adsorption of an impurity on certain crystal planes does not necessarily lead to incorporation along these planes. There are indications, mentioned above (see Section 4.2.4(b) and (c)) that lead is not included on the (111) planes of NaCl and KCl crystals, while it is on (100). However, lead modifies the habit of KCl and NaCl crystals by the appearance of large (111) faces, which is the manifestation of lead adsorption on the (111) faces. The question then can be asked: Why is lead not incorporated along the (111) planes?

Buckley (24) asked a similar question, when he gave numerous examples in which the deposition of impurity (in his case organic dyes) is on a face different from that which is modified. At the same time, of course, he reported numerous cases where habit change and inclusion occur together.
Bunn (32) presented an explanation to the phenomenon in which an impurity is sometimes built into the crystal on faces other than the face which is most retarded. He pointed out that the impurity atom or ion attached to the surface forms a complex with the surface particles of the crystal, but if more solute is crystallized round the impurity a three-dimensional complex is formed. The retardation of growth by the adsorbed impurity, according to Bunn, depends not only on the stability of the former, but also on the instability of the latter. Whenever the three-dimensioned complex is unstable and has, therefore, a higher solubility, then it is either not formed at all (i.e. not growth around it) or if formed is soon redissolved. In either case the growth is retarded. In case, however, the instability is moderate, the retardation is moderate and the growth proceeds accompanied by some inclusion of impurity. Thus, in the faces, whose growth is most retarded (because of the instability of the three-dimensioned complex), there is little if any inclusion of impurity; in the faces, whose growth is moderately retarded there is inclusion; and finally in the faces, whose growth is not affected at all because the impurity is not strongly adsorbed, there is also no impurity in the solid.

Bunn's hypothesis, however, can be tested only after data is obtained relating the inclusion of the impurity in a face to its effect on the absolute growth rate of the
same face. The above presented data can only be used to determine the effect of the impurity on the growth rate of a face indirectly, by the effect on the habit (which is simply a manifestation of the relative growth rates of the various faces).

The experimental data presented in the last sections, were obtained before (1932-1951) the modern theories on growth retardation by impurities as well as the Hall-Chernov model of non-equilibrium impurity uptake were developed (1958-1962).

Today it is generally understood that the connection between impurity adsorption and effect on growth rate on the one hand, and adsorption and impurity incorporation on the other, is more complex than was supposed.

For instance, the Sears' view has been already presented (Section 4.1.3) that mobile impurities can retard the advancement of a step without being captured by it. Hall and Chernov on the other hand (Section 4.2.3) have predicted that strongly adsorbed impurities may diffuse to the surface, even after they have been covered by other layers, if the growth rate is very slow, leaving behind a crystal with a low impurity concentration.

Therefore, it would be desirable to interpret the above data on incorporation of impurities and answer the questions posed by the foregoing investigators in the light of the recent theories of crystal growth.

This will be done after the data concerning the incorporation of impurities, obtained in the present investigation have been added.
CHAPTER 5
INTERACTION BETWEEN RADIATION AND MATTER - AQUEOUS SOLUTIONS AND CRYSTALLINE SOLIDS

The primary or direct effects of radiation on matter consist generally in the displacement of electrons (ionization), displacement of atoms from lattice sites in crystalline solids, breakage of bonds and formation of free radicals, excitation of both atoms and electrons without displacement, and the transmutation of nuclei. The secondary effects consist of further excitation and disruption of the structure by high energy electrons and atoms which have been freed by collision. The relative amounts of ionization, excitation, and displacement depend upon the kind and the energy of radiation \( (56, 14) \). In the following section the literature dealing with radiation-induced changes in an aqueous solution and on a dry crystal will be considered separately. In both cases the specific effects of each kind of radiation will be presented briefly. Finally the interaction of photon radiation with crystalline solids will be discussed in detail, since this is the kind of radiation used in the present investigation.

5.1 Effects of Radiation on Aqueous Solutions

In a dilute aqueous solution, water, which is the major component, absorbs essentially all the radiation energy. The result is the cleavage of the water molecules to free radicals \( \text{H} \) and \( \text{OH} \).* A proportion of these radicals

*Although the formulas of the free radicals are generally written \( \text{H} \) and \( \text{OH} \), their actual molecular constitution is not definitely known \( (1) \).
will recombine to form either $\text{H}_2\text{O} (\text{H} + \text{OH})$ or molecules of $\text{H}_2 (\text{H} + \text{H})$ and $\text{H}_2\text{O}_2 (\text{OH} + \text{OH})$, which are called "molecular decomposition products". (1)

In the irradiation of dilute aqueous solutions, with heavy particle radiation, the radicals formed are very close together and combine to the molecular products, before they react with the solute atoms.

In the irradiation with light particles,* on the other hand, most of these radicals diffuse into the solution and react as free radicals with whatever solutes they may find. Ultimately, the major chemical changes occur in the dissolved material, and little hydrogen or hydrogen peroxide is found. In a concentrated solution, the solute atoms may directly absorb part of the radiation energy.

The nature of the chemical change depends on the kind of the radiation and the chemical constitution of the solute. For example, $\text{KClO}_4$, $\text{KMnO}_4$, and other oxidizing agents are reduced under gamma-radiation while solutions of $\text{Sn}^{++}$ are oxidized to $\text{Sn}^{+++}$ under the same radiation. Chloride ions do not react effectively with OH in neutral solution; however, $\text{Cl}^-$ reacts with OH in acid solution, according to the following reaction (1):

$$\text{Cl}^- + \text{OH} + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{Cl}$$  \hspace{1cm} (5-1)

*Gamma-rays are included, since the agency which affects the water is in this case an electron (photoelectric or Compton).
The resulting Cl atoms either oxidize other solute ions (for instance Fe\(^{++}\), if present) or combine to form Cl\(_2\). (23,101)

Generally speaking, the specific reactions which the water radicals will produce on any given solute are not generally known a priori.

5.2 Effects of Radiation on Dry Crystals

As has already been mentioned, irradiation with fast particles (high energy neutrons, protons, electrons, etc.) or with energetic electromagnetic radiation (gamma-rays) usually results in ionization (transfer of energy to individual electrons of the solid) or displacement of atoms (transfer of energy to target atoms). The latter effect is the most significant in the growth process of crystals and it will be considered briefly in the following. A general model of radiation damage in crystals is presented first, followed by a discussion of the specific effects of each kind of radiation.

5.2.1 General Model of Radiation Damages in Crystals

A particle - neutron, electron or charged ions - moving through a crystalline solid is slowed down by numerous collisions. Some of these collisions transfer enough energy to the "struck" atom to displace it from its normal position in the lattice. In this manner a lattice vacancy is created in the crystal and, furthermore in most circumstances the recoiling atom comes to rest as an interstitial atom. For a large diversity of solid materials, the thres-
hold energy has been estimated by several authors \(^{35,58}\) to be of the order of 25 eV. This value is considerably larger than the energy, 3 to 6 eV, required to form a Frenkel defect (an interstitial-vacancy pair) by a thermodynamically reversible process \(^{15}\).

The process described above is called the primary process. The primary recoils or knock-ons, however, are frequently sufficiently energetic to produce secondary recoils and initiate in this way, a displacement cascade. This cascade ends when the energy of each particle has been degraded so that the maximum possible energy transferred in subsequent collisions is less than the threshold energy.

The model is completed with the concept of thermal and displacement spikes. The first concept of thermal spikes, is more firmly grounded, while the second, envisioned initially by Brinkman \(^{22}\), is still in a speculative state. A thermal spike is a region of particularly enhanced lattice vibrations occurring along the paths of the impinging particle and/or the primary knock-on. In other words we consider an atom or a particle moving through a lattice to transfer to another atom energy, which is not sufficient to displace it. In this case the atom starts vibrating with very large amplitude and transferring energy to its neighbors. These in turn give energy to their neighbors and so on. A localized excitation develops in the lattice
as if the lattice had been heated suddenly to a high temperature in a restricted region. Such local excitations are expected to stimulate activated processes like diffusion, nucleation, and phase change of solids which are in a metastable state with respect to another solid phase. Moreover, there are reasons to believe (52) that after cooling, an appreciable number of dislocations are left although the experimental evidence for this is equivocal.

A displacement spike is a region to be considered as molten for a very short time. Brinkman (22) first pointed out that when the energy of the primary knock-on fell below a certain value, the average spacing between secondary displacements would be of the order of one interatomic distance. This means that at the end of the track of the primary, a large number of atoms would be brought rather violently to the molten state. It is expected also in this case that dislocations would remain after the resolidification (52). In summary, irradiation of a crystal produces point defects (vacancy-interstitial pairs) and probably line imperfections (dislocations).

The general model of radiation damages in crystals is presented schematically in Fig. 5-1. It should be emphasized that this gives only a general picture of the atomic displacements by irradiation. The specific results of an irradiation, i.e. to what extent each effect (knock-on cascades, spikes, number of atoms disordered, dislocations) occurred and what additional changes are induced by
FIGURE 5-1
TWO-DIMENSIONAL SCHEMATIC REPRESENTATION OF RADIATION DAMAGE MODEL
(After Brinkman (22))
the irradiation, are determined by two factors: the nature of the crystal and the kind of radiation.

5.2.2 Neutron Irradiation

The primary result of neutron irradiation other than transmutation, is atomic displacement. Ionization appears only as a secondary process. This is because neutrons are electrically neutral and produce disturbances in a crystal lattice only when they make direct collision with a lattice atom. This primary knock-on leaves its site with so much energy that it produces a great number of secondary displacements (of the order of $10^2$) together with a thermal spike and a displacement spike. Finally the damage caused by a primary knock-on could be represented by the very model discussed above (Fig. 5-1). Transmutation is not of interest here and occurs to an appreciable extent only when materials of high neutron absorption cross-section are bombarded with neutrons.

5.2.3 Protons, Deuterons, and Other Charged Particles

Although the collision cross section is much higher for charged particles than neutrons, the former are much less effective in producing displaced atoms. The difference is largely due to the fact that charged particles passing through matter lose a very appreciable part of their kinetic energy in exciting electrons. The low value of the energy transferred to a struck atom results in a much smaller value for the number of secondary displacements
caused by the primary knock-on than in the case of neutrons; for instance 5 or 6 for a typical case of a 10 Mev charged particle as compared to about 400 for a neutron of the same energy.

Nevertheless, in spite of the small number of displaced atoms, charged particles such as deuterons or alpha-particles are effective in producing spikes and thereby in originating dislocation-like structure. Charged particles do not penetrate appreciably into the crystal. Thus the imperfections created are less homogeneously distributed than in neutron irradiation, and they are located close to the surface. In the case of bombardment with heavy ions, most of the damage is done on the first two or three layers of the crystal. (123)

5.2.4 Electron Irradiation

Electrons of energy beneath the relativistic range do not possess sufficient momentum to displace atoms in the common solid. However, electrons with energies of the order of 1 Mev can do so in head-on collisions. The energy transferred is, in all practical cases, only slightly larger than the threshold energy, and only one interstitial-vacancy pair per incident electron of about 1 Mev is produced. Spikes are not created by electron irradiation, and thereby dislocations originating from spikes are not expected. However, there is an indication that at high doses another mechanism results in structures that can act
as dislocation sources. Gilman and Johnston (80), investigating the etched surface of neutron-irradiated crystals of LiF, found several markings (a rather uniform roughening of the etched surface), which they interpreted as being caused by the presence of vacancy clusters, since it is believed that etching is not caused by individual point defects. Similar markings were observed, however, also after electron bombardment. In both cases above 400° the clusters were transformed into dislocations. They used 1.5 Mev electrons and a total dose of the order of $10^{15}$ electrons/cm².

5.3 Effect of Photons on Crystals

5.3.1 Mechanisms for the Transfer of Energy to Electrons

Photons of energy in the Mev range are capable of displacing atoms in solids. Direct interaction of a photon with atomic nuclei to produce displacements may be ruled out for energies of readily available γ-rays. Photons, however, can transfer momentum to electrons, which can in turn produce displacements.

Three processes are mainly responsible for the absorption of photons and the ejection of electrons: the photo-electric effect, the Compton effect, and pair production. For a given photon energy, the atomic cross section for each process depends on the atomic number of the absorber. The dividing lines between the processes can be given, therefore, on a diagram of atomic number vs photon energy.
In Figure 5-2 the dividing lines are drawn so that the atomic cross sections are equal for neighboring processes along the lines.

From Figure 5-2, it is seen that for x-rays the chief contribution to the absorption process comes from the photoelectric effect, except in the very light elements. In the photoelectric process all the energy of the incident...
photon is transferred to a bound electron which is ejected from the atom. At high enough energies (>5 Mev), on the other hand, the process called pair formation becomes important. In this process an electron and a positron are created by the disappearance of a γ-ray.

For γ-rays in the range 1 to 3 Mev and consequently for most reactor γ-rays, and also for γ-rays from Cobalt 60 (1.33 and 1.17 Mev) the Compton effect is the most important process, except of course for the case of very high atomic number materials.

In the Compton process, the incident photon is scattered by one of the atomic electrons which is separated from its atom. The photon moves off at an angle with

\[ E_{\gamma} \quad \text{Incident Photon} \]
\[ \phi \]
\[ \text{Scattered Photon} \]
\[ \text{Electron, } E_c \]

its original direction and with less energy than it had initially. The energy of the electron, \( E_c \), starting from 0 for \( \phi = 0^\circ \) rises up to a maximum for \( \phi = 180^\circ \).
\[ E_C(\text{Max}) = \frac{2E_\gamma^2}{m_e c^2 + 2E_\gamma} \]  

(5-2)

where \( E_\gamma \) = the energy of the incident photon
\( m_e \) = the rest mass of an electron
\( c \) = the velocity of light.

For Co\textsuperscript{60} \( \gamma \)-rays for example \( E_\gamma = 1.33 \) and the \( E_C(\text{max}) = 1.12 \) Mev. The distribution of \( E_C \) is weighted heavily toward high values of energy as it is evident from the Compton cross section per unit energy of an atom, which is given by the formula (13):

\[ \sigma_c = \frac{1}{1-\epsilon} + 1-\epsilon + \frac{\epsilon}{\gamma^2 (1-\epsilon)} \left[ \frac{\epsilon}{1-\epsilon} - 2\gamma \right] \]  

(5-3)

where \( \epsilon = \frac{E_c}{E_\gamma} \), \( \gamma = \frac{E_\gamma}{m_e c^2} \) and \( \sigma_o = \frac{E_\gamma^2}{\pi r_o^2 Zmc^2} \). Here \( Z \) is the atomic number of the sample and \( r_o \) is the "classical radius" of the electron, \( r_o = \frac{e^2}{m_e c^2} \). This distribution of \( E_c \) makes the Compton process very effective in providing electrons in the energy range for producing atomic displacements. This creation of displacements by the internal electron-irradiation will be analyzed next.

5.3.2 Displacements Produced by Gamma-Irradiation

a) Compton Mechanism

The production of a displacement by gamma-rays due to the Compton process involves three consecutive steps: (1) A photon of energy \( E_\gamma \) transfers energy \( E_c \) to an electron, which is separated from its atom, (2) the electron starting
with energy $E_c$ loses energy along its path and (3) the electron having an energy $E_e \ll E_c$ may collide with an atom transferring to it energy $E_d$. In case $E_p \gg E_d$, where $E_d$ is the threshold energy of displacement, the collision leads to atomic displacement. This displacement cross section generally can be calculated from the following (14)

$$
\sigma_d = \int_{E_d}^{E_{p \text{ (Max)}}} \sigma(E_e, E_p) dE_p
$$

(5-4)

where $\sigma(E_e, E_p)$ is the collision cross section and $E_{p \text{ (Max)}}$ is given by

$$
E_{p \text{ (Max)}} = \frac{2(E_e + 2m_e c^2)}{M c^2} E_e
$$

(5-5)

$M$ is the mass of the target atom and $E_e$ the energy of the incident electron. In order, however, to calculate the displacement cross section $\sigma_{c,d}$ of the $\gamma$-rays due to the Compton process, it is necessary to perform two additional integrations: a) an integration over the electron range to include the distribution in energy $E_e$ of electrons starting out with energy $E_c$ ($E_e$ from 0 to $E_c$) and b) an integration over $\sigma_c$ (see Equation 5-3) to include the distribution of Compton electron energies $E_c$ ($E_c$ from 0 to $E_c \text{ (Max)}$ as it is given by Equation (5-2)).

Therefore for incident $\gamma$-ray energy $E_p$

$$
\sigma_{c,d} = \int_0^{E_{c \text{ (Max)}}} \sigma_c dE_c \int_0^{E_c} N_0 \left( -\frac{dE_e}{dx} \right) dE_e \int_{E_d}^{E_{p \text{ (Max)}}} \sigma(E_e, E_p) dE_p
$$

(5-6)
where \( N_0 \) = the number of atoms per \( \text{cm}^3 \)
\[ \sigma_c \] = the Compton cross section given by Equation (5-3)
\[ \sigma(E_e, E_p) \] = the collision cross section given in the literature (119, 158)

The ratio \( \frac{dE}{dx} \) is the change of electron energy per \( \text{cm} \) of path. In computations, either experimental values may be used - if these are available - or can employ one of the proposed theoretical relations. Dienes and Vineyard (56) suggested the use of the Evans expression:

\[ -\frac{dE}{dx} = \frac{2\pi e^4 N_0 Z L}{m_0 c^2} \left(\frac{1 + E/m_0 c^2}{E}\right) \] (5-7)

where \( L \) is a coefficient depending weakly on the electron energy and the nature of the stopping material, and has a value of 10 for the usual cases of interest. With this information, Equation (5-6) can be evaluated to find the displacement cross section \( \sigma_{c,d} \) of the \( \gamma \)-rays due to the Compton process. Then the total number of atoms displaced/\( \text{cm}^3/\text{sec} \), \( R_d \), by the Compton electrons can be calculated since

\[ R_d = \phi \gamma N_0 \sigma_{c,d} \] (5-8)

where \( \phi \gamma \) is the \( \gamma \)-ray flux, photons/\( \text{cm}^2/\text{sec} \). Oen and Holmes (139) have made extensive calculations of \( \sigma_{c,d} \) for a wide range of \( E_d \), \( E_\gamma \) and \( Z \). Typical results for \( E_d = 25 \text{ eV} \) and for 1.2 Mev \( \gamma \)-rays are listed in Table 5-1 (taken from Reference 118, p. 28).
TABLE 5-1

Atomic Displacement Cross Sections via Gamma Irradiation

\[ E_d = 25 \text{ eV} \quad E_{\gamma} = 1.2 \text{ Mev} \]

<table>
<thead>
<tr>
<th>( Z )</th>
<th>( \sigma_{c,d} ) barns</th>
<th>( \sigma_{p,d} ) barns</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.114</td>
<td>1.33 x 10^{-6}</td>
</tr>
<tr>
<td>13</td>
<td>0.166</td>
<td>2.61 x 10^{-4}</td>
</tr>
<tr>
<td>22</td>
<td>0.114</td>
<td>1.83 x 10^{-3}</td>
</tr>
<tr>
<td>29</td>
<td>0.105</td>
<td>5.32 x 10^{-3}</td>
</tr>
<tr>
<td>40</td>
<td>0.0494</td>
<td>0.0135</td>
</tr>
<tr>
<td>50</td>
<td>0.0161</td>
<td>0.0200</td>
</tr>
<tr>
<td>74</td>
<td>0.000</td>
<td>0.0100</td>
</tr>
<tr>
<td>92</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

\( \sigma_{c,d} \): cross section from Compton electrons,

\( \sigma_{p,d} \): cross section due to photoelectron

In the same table the displacement cross section due to photoelectrons is presented. From the values presented, it is evident that this mechanism does not make an appreciable contribution for \( Z < 40 \) in comparison with that of the Compton process.

Experimental measurements in Ge\((Z = 32)\) irradiated in a Co\(^{60}\) source \((52)\) indicated a displacement cross section by photons of 0.015 barns which is inside the same order of magnitude with the calculated value.
Experiments, however, with alkali halides showed displacement cross sections higher than the theoretically predicted. These experiments will be discussed below, together with the mechanisms proposed to account for the high displacement cross sections.

b) Other Mechanisms for Displacement Production

There are cases, where displacements were produced, although they were not anticipated by the mechanism described above. For instance, the production of displacements in alkali halides by x-rays, which is indicated by the appearance of color centers (see Section 3.4.1), cannot be explained by direct momentum transfer. To explain this phenomenon Seitz (157) proposed that the x-rays produce excitons, that is traveling excited states of negative ions (the excited electron becomes nearly ionized, but not quite, and remains weakly bound to its "hole"). This exciton recombines and gives up its energy when it encounters perturbed regions in the crystals. Jogs in dislocation lines (see Section 3.4.3) are likely sites for such discharges, and this energy release can induce "evaporation" of vacancies from the jog. No quantitative treatment of this mechanism is available.

The second displacement mechanism was suggested by Varley (165,166), mainly for ionic crystals. According to this proposal, some negative ions lose electrons (become ionized) by irradiation with γ-rays, x-rays and charged particles and becomes positively charged. The positive ion finds itself in an unstable state...
tion and moves to an interstitial site. The displaced ions are subsequently trapped in positive ion vacancies (167).

Experiments by Varley (167) on coloration of alkali halides by X-rays are in general agreement with his model. He also observed experimentally (from optical measurements on color centers) the cross section for displacement by electron bombardment to be about 30 times larger than that for direct collision between electron and atom. (166) Since gamma-rays give rise to fast Compton electrons, they are expected to behave similarly.

Therefore, although the calculated displacement cross section for KCl would be of the order of 0.1 barn (see Table 5-1), the actual cross section is expected to be larger. Indeed Nowick (137) and Crawford and Young (53) irradiated NaCl with γ-rays from a Co\(^{60}\) source. They measured the concentration of vacancies produced by the irradiation at room temperature by determining the concentration of color centers (F-centers). The values they found correspond to a displacement cross section of from 4000 to 8000 barns (see Appendix A9).

Besides Seitz's and the original Varley's theories, others have been proposed to explain these high experimental values. All these theories attempt to explain the fact that the number of defects formed is in excess of those accountable by the momentum transfer directly to the atoms from the energetic electrons.
Klick (105) has suggested that the double ionization of a halide ion or single ionization of two adjacent halide ions leads to the formation of a neutral halogen molecule which might become localized at one halide site. Thereby an interstitial and a vacancy are formed.

Recently Williams (178) concluded that most probably two negative halogen molecule ions $X_2^-$ are formed rather than a neutral halogen molecule. This way two vacancies are formed for two single ionized halide ions.

More recently Varley (167) discussed the role of the dislocations as trapping centers for the halogen ions which are displaced under X- or $\gamma$-rays by multiple ionization. He described two cases; the one concerns displaced halogens which find themselves in the core of a dislocation; they will migrate along the core and will be trapped finally at dislocation jogs. If there is to be no charge built up at the dislocations, positive ions must also be pulled into the dislocation core. In this way, even if halogen ions alone are displaced by irradiations, dislocation climb can occur with the simultaneous creation of negative and positive ion vacancies. It should be noted that the net result is the same as in the previously discussed Seitz mechanism.

An alternative possibility for the interstitial halogen ions is to migrate along dislocations near the surface to the face of the crystal. The experimental observation
of Hibi and Yada (92), that crystallites are formed on a dry KCl crystal, which is irradiated by X-rays, can be explained this way. Varley concluded (167) that in a shell of $\sim 10^{-5}$ cm thickness near the boundaries of a crystal, some of the halogen ions displaced by multiple ionization can reach the boundary.

It has not been shown conclusively yet which of the preceding mechanisms is the most important in alkali halide crystals. It is possible that more than one process are involved each to an extent that depends probably on the nature of the crystal, the energy of the photons, the temperature and the amount of impurities incorporated into the crystal.

The last factor is a very important one. It has been recognized by many investigators (61,148) that the major cause of the contradictory data on the effect of ionizing radiation on alkali halide crystals is the presence of impurities in the crystals. The crystals used in the various investigations contained impurities at very low concentrations, nevertheless they were sufficient to affect the measurements. A characteristic example is lead which is always present in NaCl or KCl crystals. Schulman (148) pointed out that some of the effects attributed to the action of X-rays on pure KCl or NaCl crystals, result from the lead ions present inside the lattice (see next Section C).
The development, therefore, of a method for the production of crystals with much lower concentrations of impurities than the available crystals, will be helpful in the study of the effect of radiation on ionic crystals.

In Chapter 8 of this investigation such a method is suggested.

c) **Displacements in Ionic Crystals Containing Multivalent Impurities**

The electronic processes which take place in an alkali halide crystal when the crystal is gamma-irradiated become more complex if multivalent impurities are present.

One factor is the large number of charge compensating vacancies present in such a crystal. For instance, in an alkali halide containing a divalent metal ion a cation vacancy is introduced into the lattice with each divalent atom impurity in order to insure electrical neutrality. In that case, according to Varley (167), a large number of neutral halogen atoms (produced by the irradiation) are trapped in these positive ion vacancies leading to permanent coloration. If there were no positive ion vacancies, the halogen atoms would diffuse back mainly to negative ion vacancies and restore the crystal towards equilibrium.

The divalent ions are usually closely associated with the charge compensating positive ion vacancy (90). Sometimes pairs of vacancies are associated with the positive ion vacancy forming a vacancy aggregate.
Another effect of the divalent ions is to act as traps for the electrons released by the ionizing radiation. In such cases the divalent atom becomes monovalent. The associated vacancies are then freed and can migrate.

The impurity atom, in certain cases, may be reduced further to a metal atom, and may precipitate as a separate phase generally in a colloidal form. According to Schulman (148) this process occurs on x-irradiation of NaCl containing Pb$^{++}$.

The processes, however, taking place during the irradiation of a specific alkali halide crystals containing a specific multivalent impurity cannot be predicted a priori. Only investigation of the system through certain physical measurements, like conductivity measurements or measurements on optical absorption spectra and ESR spectra, can provide information regarding the electronic processes which actually take place.
EXPERIMENTAL PROCEDURE FOR THE GROWTH OF CRYSTALS

The experimental procedure for the growth of the potassium chloride crystals and the measurement of their growth rates is described in this Chapter.

The experimental procedures involved in the etching of the grown crystals and the determination of the impurities incorporated into them are described in Chapters 8 and 9, where the results of these two studies are also presented.

The experimental procedure for the growth of crystals consisted of the following main steps.

1) Saturation of the solution
2) Preparation of seed crystals
3) Growth on the crystal seeds from pure solutions and from solutions containing additives
4) Growth on the seeds from solutions under gamma irradiation
5) Measurement of the crystal dimensions after growth and recording of the growth rates.

6.1 Saturation of the Solution

6.1.1 Materials

The potassium chloride used in this investigation was obtained from the Baker Chemical Company. It was in the form of crystalline powder and was of reagent grade ("Baker Analyzed"). The analysis reported by Baker Chemical Company
is given in Appendix A2.

Distilled water corresponding in purity to triple distilled (distilled water distilled further in a Barnstead still including a "high purity" section) was used throughout the investigation (measured specific resistivity about 1 Mohm).

6.1.2 Saturation Procedure

Potassium Chloride in excess of that required to make about 1500 cc of saturated solution at the desired temperature was added to triple distilled water in a two liter volumetric flask. This was left in a constant temperature bath for at least 18 hrs., under vigorous stirring of the contents with a magnetic stirrer. The magnetic rod inside the solution was teflon coated. The variation in the temperature of the bath was kept within 0.01°C by using an external infrared heater which was connected to a temperature control relay. (See Figure 6-1)

The saturated solution was transferred to the crystallizer by using a glass transfer tube. The end of the tube placed in the flask consisted of a sintered glass filter to prevent carryover of undissolved crystals. The outside portion of the tube was wrapped with a heating tape and heated to a temperature of 10 to 20°C higher than the saturation temperature in order to avoid any crystallization by cooling at the tube-wall.

A slight pressure of pre-purified nitrogen was used to force the saturated solution through the porous plug
and the heated portion of the tube into the crystallizer flask.

The saturation temperature was usually adjusted so that the desired supersaturation would be obtained at a constant growth temperature of 35.00°C.

6.2 Preparation of Seed Crystals

The small KCl seed crystals of rectangular parallelepiped form were cleaved from large crystals obtained by crystallization from melt of analytical grade KCl. These crystals were obtained from the Insulation Laboratory of MIT. A pair of fine tip stainless steel tweezers and a stainless steel razor blade were used for the cleavage. The seeds were mounted on a stainless steel holder (a pair of very fine tweezers) so as to provide a means of suspension inside the flask. In some runs a glass holder was employed, (these runs are indicated in the table of results, Appendix A14).

The crystals were held across the dimension here called "width", W, while they were free to grow along the "length", L, and "height", H, dimensions (see Figure 6-2). The crystal was oriented inside the solution in such a way that the direction of the flow was parallel to the faces, which are not touched by the holder, i.e. H and W faces.

After the attachment of the seed to the holder, its three dimensions were measured under a microscope (50X magnification). The eyepiece lens had a calibrated scale
FIGURE 6-1
SCHEMATIC DIAGRAM OF EQUIPMENT

solution to crystallizer flask

SATURATION FLASK

solution

CRISTALLIZER FLASK

N₂

constant temperature bath

heating tape

thermoregulator

infrared heater

crystals

sintered glass filter

magnetic stirrer

tweezers

thermoregulator

constant temperature bath

infrared heater

crystals

supersaturated solution
FIGURE 6-2
ATTACHMENT OF A CRYSTAL SEED TO THE HOLDER
of 100 units, each of which corresponded to 24.7 microns. The linear dimensions of the seeds were usually between 40-90 scale divisions, i.e. from 1 mm to about 2 mm.

6.3 Procedure for the Growth of the Crystals

6.3.1 Apparatus

The design of the apparatus permitted growth of one or two crystals, under vigorous stirring and at any constant level of supersaturation, temperature and additive concentration desired.

A schematic diagram of the apparatus is presented in Figure 6-1. A 1000-ml three-neck crystallizer flask was immersed in a water bath. The temperature in the crystallized was maintained constant by regulating the temperature of the bath within ±0.01°C. The use of infrared heaters (250 W) was very helpful in maintaining such a small temperature fluctuation.

The temperature of the bath was indicated by a Beckman differential thermometer readable to 0.005°C. This Beckman thermometer was calibrated against a graduated thermometer indicating tenths of a degree. The latter had been calibrated against another thermometer checked in the National Bureau of Standards.

Since, the calibrated thermometer was readable to 0.05°C, the precision of the value given by the Beckman thermometer was ±0.05°C. This systematic error, however, was kept constant throughout this investigation by calibra-
ting all the employed Beckman thermometers* against the first one. This means, that when a crystallization temperature of 35°C is reported, this value is accurate within ±0.01°C but precise within ±0.05°C. Nevertheless in the calculation of supersaturations from the difference between the temperature of the saturation bath and the temperature of the growth bath, the above systematic error is, obviously, cancelled out.

Stirring was provided in the crystallizer by a variable speed stirrer having either a type 316 stainless steel shaft or a glass shaft (the latter was employed in the runs indicated by the letter G and a number; see Appendix A14). The shaft was attached to the stirrer through a sealed bearing at the cover of the flask. Thus evaporation of the water was prevented and the concentration of the solution remained constant (the amount of salt crystallized in a run was a negligible fraction of the total dissolved salt).

A recycling flow apparatus was used for a small number of runs (indicated by the letter S and a number). This apparatus is described in details in Appendix A15. It has certain merits in comparison to that shown in Fig. 6-2 and will be recommended for use in future experiments of crystal growth.

6.3.2 Growth Procedure

The crystallizer flask was always filled to the same level with solution transferred from the saturation flask.

*Also the thermometers used in the investigations by Garavito (77) and Sanni (145).
Then the temperature of the bath was raised to 2 to 3 degrees above the saturation temperature and held at this level for 45 to 60 minutes to assure the dissolution of any crystal formed during the transfer operation. The solution was cooled slowly to the desired growth temperature and maintained at this level for at least one hour before the introduction of any seed. The lengths of time mentioned above were dictated by the time lag and thermal response of the crystallized-bath system.

The crystal holders were then inserted into the supersaturated solution through the side necks of the flask and the growth of the seeds proceeded under conditions of constant temperature and supersaturation. After a growth period sufficient for each dimension of the seed to increase about 0.5 mm, the holder with the grown crystal was removed from the solution.

The crystal was dried by touching it carefully with filter paper and its dimensions were measured under the microscope, without removing it from the holder.

The depletion of the solution by the growing crystals with respect to both crystallizing species (KCl) and additives, was negligible. Pertinent calculations are included in Appendix A3.2.

When the growth of crystals in the presence of impurities was studied, the impurity was introduced before the initiation of the procedure mentioned above.
6.3.3 Addition of Impurities

The necessary amount of impurity was added from a stock solution by means of a buret or a micropipette. The concentration of the solution was such that only the smallest possible volume was added in order not to change the concentration of the crystallizing solution by addition of excess water. Most of the time one drop of solution of additive was sufficient.

When high concentrations of impurities were desired (for example $10^{-5}$ moles/mole KCl), the additive salt was either added directly into the solution, or a certain amount of a concentrated solution was added and the necessary corrections in the supersaturation were made.

6.3.4 Cleaning Procedure

All glasswares were cleaned with chromic acid cleaning solution ($\text{H}_2\text{SO}_4-\text{K}_2\text{Cr}_2\text{O}_7$) and rinsed repeatedly with triple distilled water. When an additive had been used, the glassware was cleaned with an acid forming a very soluble salt with the additive, (for instance nitric acid for Pb$^{++}$) before using the chromic acid cleaning solution.

After rinsing with water, the transfer tube and the crystallizer flask were rinsed with reagent grade acetone and dried by blowing pre-purified nitrogen gas through them.

6.4 Growth Procedure under Irradiation

6.4.1 Radiation Source

The Co$^{60}$ source, located at the Department of Nutrition and Food Science of MIT was used.
A diagram of the Co\textsuperscript{60} gamma-rays source is shown in Figure 6-3. It consists of a tank 12 feet deep, filled with water. The Co\textsuperscript{60} pellets are sealed inside cylinders, which are placed in racks at the bottom of the tank.

The assembly containing the material to be irradiated is placed in a lug. The lug is introduced inside one of the containers (Figure 6-4) and fastened so that a watertight metallic box is formed (Figure 6-5). This box is finally lowered inside the well. Sections of tygon tubing, connected tightly to the top of the box and reaching above the surface of the water shielding, act as channels through which pass the electrical wiring, thermocouple wiring, cooling water tubing, etc.

In this source a maximum dose rate of about 4500 rad/min can be obtained in certain sections of the center container. The outer two containers receive about 2500 rad/min. The dose rate received by crystallizer flask is determined in Appendix A3.5. It was estimated to be 2400 rad/min.

6.4.2 Apparatus for Growth under Irradiation

The same type of crystallizer flask was used as in the experiments conducted without irradiation. It was immersed in a constant temperature water bath. (Figure 6-6). The differences between the two set-ups i.e. with and without irradiation, were the following; a rectangular bath was employed in the former case in order to fit
TANK
12 feet deep filled with water

LUG CONTAINER

CRYSTALLIZER FLASK IN THE LUG

FIGURE 6-3
SCHEMATIC DIAGRAM OF RADIATION SOURCE
FIGURE 6-4
LUG BEING LOWERED INTO THE LUG CONTAINER
(Lug contains the constant temperature bath of crystallization)

FIGURE 6-5
LUG WELL TIGHTENED, READY TO BE LOWERED INTO THE RADIATION WELL
FIGURE 6-6
CONSTANT TEMPERATURE BATH FOR THE EXPERIMENTS UNDER IRRADIATION

A : Thermoregulator
B : Resistance thermometer
C : Crystallizer flask
D : Crystal holder
E : Infrared heater
F : Coil for cooling water
G : Stirrers
inside the lug; the output of the heater, as well as the heat resulting from the gamma-rays absorbed by the water of the bath, was balanced against heat removed by water flowing in a cooling coil; finally, for the experiments under irradiation, the temperature is sensed by a platinum resistance sensor (Rosemount Engineering Company, Model 104F). This is made of platinum wire hermetically sealed within a thin stainless steel sheath and has an accuracy $\pm 0.03^\circ C$. The sensor was immersed in the solution of the crystallizer-flask. The temperature inside the crystallizer was recorded by a Honeywell strip chart recorder.

Measurements of bath temperature indicated that a given constant temperature was maintained by the bath at the same level both in and out of the radiation field (see also calculations in Appendix A3.4).

6.4.3 Procedure for Growth under Irradiation

The procedure was the same as in Section 6.3.2 up to the point of introduction of the crystal seeds. In the growth experiments under irradiation, immediately after the introduction of the seeds, the water bath was placed inside the container. Then the bolts were fastened and the watertight metallic box was lowered in the water tank and at the desired level. This was close to the bottom of the tank for maximum radiation dose rate and just underneath the surface of the water for check runs at practically zero dose rates.
6.5 Measurements of Crystal Dimensions and Supersaturation

6.5.1 Crystal Dimensions

The potassium chloride crystal can be cleaved only along the (100) faces. The seeds, therefore, contained only (100) faces (Figure 6-7).

The initial "length" $L_0$ and the "height" $H_0$ of the seed crystals were measured under the microscope.

After the growth the dimensions $L$ and $H$ were measured again. The average of the two differences $L-L_0$ and $H-H_0$ divided by 2 gave the advancement of an (100) face of the crystal. Dividing this number by the time of growth gives the growth rate (length/time) normal to an (100) face.

The measurement procedure is described in detail in Appendix A3.1.

It should be noted that the grown crystals contained not only the (100) faces but also (111) and sometimes (110) faces. (see Figures 6-7 and 6-8). The investigation, however, was confined into the study of growth rates along the (100) faces only.

6.5.2 Supersaturation

The supersaturation is given by

$$ S = \frac{C_L-C_0}{C_0} $$

(6-1)

where $C_L =$ actual solution concentration

$C_0 =$ solubility at the crystallization temperature

The supersaturation during a growth experiment was calculated from the temperature of the saturation bath and
CRYSTAL HABIT OF POTASSIUM CHLORIDE

Points at which the crystal was held by the tweezers

(100) face (perpendicular to the plane of the picture)

FIGURE 6-8
GROWN CRYSTAL OF POTASSIUM CHLORIDE
the temperature of the growth bath coupled with the solubility data; i.e. the solubility at the saturation temperature gives $C_L$ while the solubility at the growth temperature gives $C^0_L$.

The solubility data used in this investigation are reported in Appendix A1.

6.6 Accuracy of the Measurements

6.6.1 The Determination of Growth Rates

The growth rates were determined by dividing the difference of the measured initial and final lengths of the crystal faces by the growth time.

The uncertainty in the time of growth was rather small, since the duration of growth was from 1 to 8 hours.

The measurements of the two lengths (initial and final) were the main contributions to possible errors in growth rate determination. It was estimated that the error in measuring a dimension of a seed crystal was $\pm 0.5$ scale divisions while for a grown crystal was $\pm 1.0$. The absolute error in total growth (given by the difference of the two measured lengths) was therefore conservatively $\pm 1.5$ scale divisions, i.e. $\pm 37.0\mu$.

The accuracy in growth rate is given for all values presented in the tabulation of data (Appendix A14). It was obtained by converting the accuracy of the total growth ($\pm 37.0\mu$) to the basis of growth rate per face.

Since the estimated absolute error is constant, the estimated relative error is greatest for little growth.
6.6.2 The Determination of Supersaturation

The supersaturation of the solution in contact with the crystal was fixed by the saturation temperature, the growth temperature, and by the equilibrium solubilities at those temperatures. The accuracy of the solubility data were unknown (155); however, each temperature was constant to ± 0.01°C. For the difference of the two temperatures, the accuracy would be of the order of ± 0.02°C. Since the absolute error was constant, the percentage error in supersaturation determination was strongly dependent on the supersaturation level; for instance the error is as high as 20% for supersaturations corresponding to Δt = 0.1°C (Δt = saturation temperature - growth temperature) and as low as 2.5% for Δt = 0.8°C.

Errors in supersaturation determination could be also attributed to changes in solution concentration during the experiment: depletion of the solution by the growing crystals. Calculation (see Appendix A3.2) showed that the error would be of the same order of magnitude as that due to the temperature variation.

6.7 Features of the Experimental Procedure

In summary, the procedure involved the growth of single crystals from small seeds under conditions of constant temperature, constant supersaturation and constant additive concentration.

The crystal was held stationary inside the solution while stirring forced the solution to pass the crystal at
velocities depending upon the stirring rate. The stirring rate was varied from low values to high values, at which mass transfer of the potassium chloride or the additive through the liquid was not the controlling step (see Section 7.1.3c).

From the difference in the crystal dimensions before and after growth over the duration of growth, the growth rates normal to each face were calculated.
CHAPTER 7
RESULTS AND DISCUSSION
GROWTH RATES OF POTASSIUM CHLORIDE CRYSTALS
WITHOUT IRRADIATION

This chapter is divided in two parts. Part 7.1 deals with solutions in which no impurities were added. Part 7.2 deals with solutions containing added PbCl₂. Some data, concerning growth from solutions in which other ionic impurities were added, are summarized in Appendix A15.2.

7.1 Growth Rates from Solutions without Added Impurities

7.1.1 General—Previous Data

In order to investigate the effect of gamma irradiation on the growth rate of KCl from solutions containing no added impurities, growth rate data for such solutions without irradiation were necessary.

Previous investigations on KCl crystallization were not helpful. The data reported were either qualitative (180), or they were obtained under such experimental conditions that they were irrelevant to this investigation. Komarova and Figurovskii (108) have measured growth rates of KCl from solutions, however, the supersaturation was not constant during the crystallization, the purity of the raw material (an important factor as it will be shown below) is not specified, and the stirring was not adequate. In addition, the increase in the weight of the crystal was used to measure growth rate. This obviously cannot signify
what was the growth rate on each of the faces of the crystal: namely, (100), (110) and (111).

For these reasons an extensive investigation of the growth of KCl from solutions without additives was conducted.

7.1.2 Results

a) Reproducibility of the Data

In order to test the reproducibility of the growth rate data and at the same time point out the sources of observed fluctuations, the following experiments were performed.

1. Effect of the crystal seed. The first question concerns the effect of the seed on the reproducibility of the data. Does the growth rate vary from seed to seed? To answer this question, pairs of seeds were grown simultaneously inside the same solution and for the same period of time.

The results of growth experiments for various pairs of crystals are presented in Table 7-1.* The accuracy of the growth rate measurements is also presented for comparison with the variation between crystals of the same pair.

2. Reproducibility inside the same solution. Experiments were conducted to determine whether the growth on a

* All growth rates reported in this investigation refer to the (100) faces of the potassium chloride crystals.
Table 7.1
Reproducibility in Growth Rate Measurements
(Pairs of Crystal Growing Simultaneously inside the Same Solution)

1 Unit = 24.7 Microns

<table>
<thead>
<tr>
<th>Run</th>
<th>Growth Rate &quot;units&quot;/hr</th>
<th>Difference Between the Two Growth Rates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crystal I</td>
<td>Crystal II</td>
</tr>
<tr>
<td>A-22</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>A-23</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>A-24</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>A-25</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>A-26</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>A-27</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>A-28</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td>A-30</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>A-37</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>A-39</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>A-44</td>
<td>7.1</td>
<td>6.7</td>
</tr>
<tr>
<td>A-45</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>A-46</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
<td>A-50</td>
<td>1.7</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>1.4</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>1.4</td>
</tr>
<tr>
<td>G-12</td>
<td>5.0</td>
<td>4.5</td>
</tr>
<tr>
<td>G-13</td>
<td>4.8</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>2.6</td>
<td>2.8</td>
</tr>
<tr>
<td>G-14</td>
<td>5.0</td>
<td>5.3</td>
</tr>
<tr>
<td>G-15</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>G-17</td>
<td>0.25</td>
<td>0.32</td>
</tr>
<tr>
<td>G-26</td>
<td>1.0</td>
<td>0.75</td>
</tr>
<tr>
<td>G-28</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>G-33</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>G-34</td>
<td>1.9</td>
<td>2.0</td>
</tr>
<tr>
<td>B-39</td>
<td>6.6</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>5.9</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>5.8</td>
</tr>
</tbody>
</table>
certain seed was linear with the time. A non-linearity would indicate either changes in the solution or the existence of a resistance in growth presented initially by the surface of the seed (possible contamination). The question of whether the growth rate is constant is important since the growth rates were obtained by dividing total growth by the time of growth.

Consequently, crystals were grown from the same solution for different growth periods and at different times. The usual procedure was to keep a crystal seed on one holder for a long time, while other crystals were being grown successively in the other holder for shorter periods.

The results of these experiments are presented in Table 7-2 and plotted in Figure 7-1.

3. Variations in growth rates obtained from different solutions. Each solution could not be used in the crystalizer flask for more than 18-24 hours without extensive nucleation occurring. In addition, only a limited number of crystals could be grown without changing the concentration of the supersaturated solution. For this reason a fresh solution was used for each run. The question therefore arose on how reproducible the growth rate measurements were from solution to solution.

The average growth rates for various supersaturation levels, obtained from various solutions, are therefore presented in Table 7-3. All runs made at a certain
<table>
<thead>
<tr>
<th>Run</th>
<th>Duration of Growth Hours</th>
<th>Holder 1</th>
<th>Growth Rate of (100) Faces</th>
<th>Holder 2</th>
<th>Growth Rate of (100) Faces</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Run A-47)</td>
<td>2</td>
<td>39.5±20</td>
<td>20 ± 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Super-</td>
<td>3.5</td>
<td>69.0±17.5</td>
<td>20 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>saturation</td>
<td>0.12%</td>
<td>2</td>
<td>44.5±20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solution 2</td>
<td>2.5</td>
<td>154±22.5</td>
<td>62 ± 9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Run A-48)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Super-</td>
<td>2.5</td>
<td>154±22.5</td>
<td>62 ± 9</td>
<td>5</td>
<td>321 ± 25</td>
</tr>
<tr>
<td>saturation</td>
<td>0.16%</td>
<td>2.5</td>
<td>172±22.5</td>
<td></td>
<td>64 ± 5</td>
</tr>
<tr>
<td>Solution 3</td>
<td>1</td>
<td>99 ± 20</td>
<td>99 ± 20</td>
<td></td>
<td>396 ± 20</td>
</tr>
<tr>
<td>(Run A-41)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>99 ± 5</td>
</tr>
<tr>
<td>Super-</td>
<td>2</td>
<td>202±20</td>
<td>101 ± 10</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>saturation</td>
<td>0.20%</td>
<td>1</td>
<td>87.5±20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
EACH POINT REPRESENTS A DIFFERENT CRYSTAL. EACH LINE REPRESENTS A DIFFERENT SOLUTION & A SUPERSATURATION S.
- O S=0.12%
- △ S=0.16%
- □ S=0.20%

FIGURE 7-1
GROWTH OF (100) FACES AS A FUNCTION OF TIME
### Table 7-3

**Average Growth Rates (μ/hr) at Various Supersaturation Levels for Various Solutions**

(Each run represents a different solution)

**Stirring Rate:** 800 - 1100 RPM

#### A. Glass Shaft and Crystal Holder

<table>
<thead>
<tr>
<th>Supersaturation Level</th>
<th>Run</th>
<th>0.09%</th>
<th>0.12%</th>
<th>0.16%</th>
<th>0.20%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G-9</td>
<td>136 ± 27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-10</td>
<td>74 ± 27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-11</td>
<td>108 ± 35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-12</td>
<td>62 ± 27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-13</td>
<td>105 ± 18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-14</td>
<td>Dendritic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-15</td>
<td>Dendritic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-16</td>
<td>Dendritic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-17</td>
<td>76 ± 15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-18</td>
<td>45 ± 15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-23</td>
<td>154 ± 18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-24</td>
<td>Dendritic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-27</td>
<td>68 ± 7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-29</td>
<td>Negligible</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-30</td>
<td>19 ± 9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-31</td>
<td>Negligible</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-32</td>
<td>Dendritic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-33</td>
<td>49 ± 9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-34</td>
<td>Negligible</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-35</td>
<td>Dendritic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-36</td>
<td>Dendritic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-37</td>
<td>Dendritic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-38</td>
<td>Dendritic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-39</td>
<td>Dendritic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-40</td>
<td>Dendritic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>G-41</td>
<td>Dendritic</td>
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<td></td>
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<td></td>
<td>G-42</td>
<td>Dendritic</td>
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<td></td>
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<td>G-43</td>
<td>Dendritic</td>
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<td></td>
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<tr>
<td></td>
<td>G-45</td>
<td>Dendritic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-46</td>
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<td></td>
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<td>G-47</td>
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<td></td>
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<td>G-48</td>
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</tr>
<tr>
<td></td>
<td>G-49</td>
<td>Dendritic</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7-3 (Cont.)

B. Stainless Steel Shaft and Crystal Holder

<table>
<thead>
<tr>
<th>Supersaturation Level</th>
<th>Run</th>
<th>0.09%</th>
<th>0.12%</th>
<th>0.16%</th>
<th>0.20%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25 ± 5</td>
</tr>
<tr>
<td>A-20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>54.5 ± 2.5</td>
</tr>
<tr>
<td>A-21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Dendritic</td>
</tr>
<tr>
<td>A-25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21 ± 5</td>
</tr>
<tr>
<td>A-27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>41 ± 5</td>
</tr>
<tr>
<td>A-28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>33.5 ± 5</td>
</tr>
<tr>
<td>A-30</td>
<td></td>
<td>7.5 ± 2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>37 ± 5</td>
</tr>
<tr>
<td>A-39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>48 ± 5</td>
</tr>
<tr>
<td>A-40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21 ± 6</td>
</tr>
<tr>
<td>A-41</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>97 ± 15</td>
</tr>
<tr>
<td>A-42</td>
<td></td>
<td>48.5 ± 6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-43</td>
<td></td>
<td>15 ± 6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-44</td>
<td></td>
<td>52 ± 7.5</td>
<td>69 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-45</td>
<td></td>
<td>32 ± 7.5</td>
<td>79 ± 12.5</td>
<td></td>
<td>Dendritic</td>
</tr>
<tr>
<td>A-46</td>
<td></td>
<td>30 ± 5</td>
<td>86 ± 10</td>
<td></td>
<td>Incipient</td>
</tr>
<tr>
<td>A-47</td>
<td></td>
<td>20.5 ± 7</td>
<td></td>
<td></td>
<td>Dendritic ~160</td>
</tr>
<tr>
<td>A-48</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>64 ± 7</td>
</tr>
<tr>
<td>A-50</td>
<td></td>
<td>34.5 ± 10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-10</td>
<td></td>
<td>89 ± 10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-12</td>
<td></td>
<td>101 ± 10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-17</td>
<td></td>
<td>37 ± 10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-18</td>
<td></td>
<td>116 ± 12.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-20</td>
<td></td>
<td>44.5 ± 10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-39</td>
<td></td>
<td>150 ± 15</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
supersaturation level could be expected to give the same value of growth rate.

The notation dendritic indicates a very fast growth resulting in dendrites (non-layer growth). Measurement usually was not possible, because the dendritic crystal did not present a definite edge. It has been concluded, however (see discussion below), that the growth rate above which dendritic growth occurs for the supersaturation level prevailing in the experiments is about 160 \( \mu/\text{hr} \).

b) Effect of Stirring Rate on Growth Rate

The effect of stirring rate on the growth rate was studied by growing crystals at different stirring rates and in the same solution.

The purpose of these experiments was to determine the conditions at which mass transfer processes through the surrounding liquid were not controlling the crystal growth rate, that is, the growth rate was independent of the stirring rate.

The results for two solutions, one giving a slow growth (curve B) and the other a very fast rate close to dendritic (curve A), are presented in Figure 7-2.

c) Effect of Supersaturation on Growth Rate

Crystals were grown at various supersaturations in the same solution. Supersaturation was varied by varying the temperature of crystallization.

The growth rate values as a function of supersaturation are presented in Table 7-4 and plotted for each
Table 7-4

Variation of Growth Rate with Supersaturation in the Same Solution

For (100) faces of KCl

<table>
<thead>
<tr>
<th>Run</th>
<th>Crystallization Temperature, °C</th>
<th>% Supersaturation</th>
<th>Growth Rate Microns/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-44(1)</td>
<td>35.00</td>
<td>0.20 ± 0.01</td>
<td>Dendritic (~173)</td>
</tr>
<tr>
<td></td>
<td>35.05</td>
<td>0.16 ± 0.01</td>
<td>70 ± 5</td>
</tr>
<tr>
<td></td>
<td>35.10</td>
<td>0.13 ± 0.01</td>
<td>52 ± 7.5</td>
</tr>
<tr>
<td>A-45(1)</td>
<td>35.00</td>
<td>0.20 ± 0.01</td>
<td>Dendritic</td>
</tr>
<tr>
<td></td>
<td>35.05</td>
<td>0.16 ± 0.01</td>
<td>79 ± 12.5</td>
</tr>
<tr>
<td></td>
<td>35.10</td>
<td>0.13 ± 0.01</td>
<td>32 ± 7.5</td>
</tr>
<tr>
<td>A-46</td>
<td>35.10</td>
<td>0.13 ± 0.01</td>
<td>89 ± 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>84 ± 10</td>
</tr>
<tr>
<td></td>
<td>35.15</td>
<td>0.10 ± 0.01</td>
<td>27 ± 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>32 ± 5</td>
</tr>
<tr>
<td>G-18(2)</td>
<td>35.00</td>
<td>0.12 ± 0.01</td>
<td>132 ± 15</td>
</tr>
<tr>
<td></td>
<td>35.10</td>
<td>0.09 ± 0.01</td>
<td>76 ± 15</td>
</tr>
</tbody>
</table>

(1) The solutions in both runs A-44 and A-45 were from the same saturated solution divided into two crystallizer flasks.

(2) In this run the shaft and the crystal holder were glass.
For instance, the growth rates obtained at 0.12% supersaturation (from negligible to 160 µ/hr) have been determined on the assumption that the supersaturation in each solution was in agreement with the theoretical values.

The data was always prepared to ensure that the growth rates were consistent with the experimental conditions.

Figure 7-2 shows the growth rates of KCl (NO PbCl₂ added) vs. stirring rate (RPM). Each curve represents a different solution.

Supersaturation: 0.12% for each curve. Curve A: Run B-39, Curve B: Run A-50.
FIGURE 7-3
GROWTH RATE AS A FUNCTION OF SUPERSATURATION

CURVES A, B, C: NO PbCl₂ ADDED
CURVE D: 1x10⁻⁷ MOLES PbCl₂ / MOLE KCl
EACH CURVE REPRESENTS A DIFFERENT SATURATED SOLUTION
EACH POINT REPRESENTS A DIFFERENT CRYSTAL
+ SHOW ESTIMATED ERRORS

DENDRITIC GROWTH REGION

GROWTH RATE OF (100) FACE MICRONS/HR

PER CENT SUPERSATURATION
For instance, the growth rates obtained at 0.12% supersaturation, from the various solutions presented in Table 7-3, indicate a considerable scattering. Growth rates ranging from negligible (\(<1\ \mu/hr\)) up to dendritic growth (\(>160\ \mu/hr\)) have been recorded, while the same value should be obtained.

Despite all efforts in refinement of the experimental procedure, this scattering of the data was always present in the growth experiments from "pure" solutions.

There are two factors that may account for the poor reproducibility obtained:

a) Errors involved in the determination of the supersaturation in each solution and

b) Differences in the purity of the growth solutions.

It was shown in Section 6.6.2 that a constant absolute error is involved in the determination of the supersaturation. The magnitude of this error, for growth experiments around 35°C, is \(\pm 0.01\).

Inspection of curves A, B and C in Figure 7-3 shows that this variation in supersaturation can account for only a 10 \(\mu/hr\) variation in growth rate at low growth rates; however, it can be responsible for a variation of 60 \(\mu/hr\) at high growth rates, due to the steepness of the curve.
solution in Figure 7-3 (Curves A,B,C).

The runs A-44 and A-45 were conducted in two different crystallizers, but the solutions for both came from the same saturation flask. The points from both these runs fit the same curve in Figure 7-3 (Curve C).

7.1.3 Discussion of the Results

a) Reproducibility of the Data

Difference in the Seeds. It is evident from Table 7.1 that the variation in growth rates of (100) faces obtained from two crystals growing simultaneously in the same solution is within the accuracy of the measurements. (Compare the last two columns of the table.) Therefore the condition of the seed surface (i.e., the smoothness of the surface, contamination of the surface during handling, scratches developed during the attachment of the seed in the holder, etc.) did not affect the growth rate appreciably.

Reproducibility Inside the Same Solution. An inspection of Figure 7-1 indicates that at a given supersaturation, the growth rates of the various crystals, grown successively in a solution, were the same (within the accuracy of the measurements), irrespectively of the duration of growth.

Reproducibility Between Different Solutions. Growth rate measurements, however, at a given supersaturation inside various solutions, showed very poor reproducibility.
The greater variation, however, observed from solution to solution suggests that: variation in the purity of the growth solutions is an important consideration.

b) Variations in the Purity of the Growth Solutions

The possible factors that may account for a variation in impurity content among the various solutions are:

1. Introduction of impurities during the transfer of the saturated solution or during the growth.

2. Impurities contained in the initial potassium chloride reagent used for the preparation of the saturated solution.

3. Variation in impurity content due to the saturation procedure.

Introduction of Impurities. Impurities could be introduced either accidentally or from the stainless stirrer shaft and crystal holder.

It became evident during the course of the investigation that higher growth rates were obtained at a given supersaturation when no metal parts were in contact with the solution than when stainless steel shaft and crystal holders were used. For instance, when glass shaft and holders were used, dendritic growth was obtained in five out of fifteen runs at a supersaturation of 0.12%. (See Table 7-3.) However, no dendritic growth was observed in any run at this supersaturation level when stainless
steel parts were used. Actually, in that case dendritic growth occurred only when the supersaturation was raised to 0.20%.

Another way to show this retarding effect of stainless steel on the growth rate is the following: The growth rate values from Table 7-3 are plotted in Figure 7-4. This figure is similar to Figure 7-3, in the respect that both indicate growth rates as a function of supersaturation. The difference, however, is that in Figure 7-4, in almost all the runs, only one point for each solution is recorded, while in Figure 7-3 growth rate values at different supersaturations for each solution are available; thereby, in the latter figure, curves "growth rate vs. supersaturation" could be drawn for each solution.

However, one can visualize in Figure 7-4 curves of the same form as the curves A, B and C in Figure 7-3. These curves would represent in Figure 7-4 growth rates as a function of supersaturation for each mother solution ("iso-solution" curves).

One such curve in Figure 7-4 is curve D, which has been drawn in such a way that it divides the graph in the following two parts: the left part where most of the points (as well as the "iso-solution" curves passing through them) representing growth with a glass shaft are lying; and the right part where most of the points (as well as the "iso-solution" curves) representing growth...
DENDRITIC GROWTH REGION

△ GLASS SHAFT & CRYSTAL HOLDER
O STAINLESS STEEL SHAFT & CRYSTAL HOLDER
EACH POINT REPRESENTS A DIFFERENT SOLUTION

GROWTH RATE OF (100) FACE

PER CENT SUPERSATURATION

FIGURE 7-4 AVERAGE GROWTH RATES AT VARIOUS SUPERSATURATION LEVELS
with a stainless shaft are lying. Since the "iso-solution" curves in the right part represent solutions showing slow growth, it is concluded that the use of stainless steel parts in the growth apparatus results in growth retardation.

This retardation could only be explained by the introduction of impurities through corrosion of the stainless steel shaft and crystal holders. The amount of impurities they introduced could vary from run to run depending on the surface conditions of the shaft or the crystal holder. This could account for the variations in growth rates in runs with stainless shafts. However, the scattering is observed also when an all glass apparatus was used. It seems, therefore, that another factor, namely the variation in the purity of the initial potassium chloride reagent, is important.

**Impurity Content of KCl Reagent.** The analysis given by the manufacturer shows that the KCl reagent contains various impurities in amounts ranging from 1 ppm up to 30 ppm (Appendix A2). At least one of the impurities, namely Pb, has an appreciable effect on the growth rate of KCl crystal. (See section 7.2.) Lead will be used as an example in the present discussion.

The manufacturer indicates that the amount of heavy metals, including Pb, which are contained in the reagent are less than 2 ppm. The exact amount of Pb contained is very difficult to be determined analytically at such a low level.
However, the property of Pb$^{++}$ to retard the growth of KCl crystals can be employed to estimate the lead content. Crystals were grown in a solution to which successively increases amounts of PbCl$_2$ were added; the growth rates of the crystals were measured. The concentration of added PbCl$_2$ at which the growth rate started decreasing indicated the order of magnitude of Pb concentration present initially. The results of such an experiment are presented in Table 7-5.

**Table 7-5**

Growth Rates of KCl Crystals in a Solution after the Addition of PbCl$_2$ (in μ/hr)

(Run G-49)

<table>
<thead>
<tr>
<th>Concentration of Added PbCl$_2$ Moles/Mole KCl</th>
<th>Supersaturation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.06%</td>
</tr>
<tr>
<td>0</td>
<td>64 ± 10</td>
</tr>
<tr>
<td>1 x 10$^{-9}$</td>
<td>52 ± 2</td>
</tr>
<tr>
<td>1 x 10$^{-8}$</td>
<td>18 ± 1</td>
</tr>
</tbody>
</table>

These results indicate that the initial concentration of PbCl$_2$ in the reagent was of the order of 1 x 10$^{-8}$ moles/mole KCl (at least for the KCl used in these experiments).
For reasons explained in Chapter 8, the average lead content of the reagent KCl is expected to vary from bottle to bottle, but always within the magnitude of $10^{-8}$ moles/mole KCl; for instance, it could very easily vary from $1 \times 10^{-8}$ moles/mole KCl in one bottle to $2 \times 10^{-8}$ or $0.5 \times 10^{-8}$ in another.*

This raises the question: can this magnitude of impurity content variation adequately account for the observed discrepancy in growth rates (Table 7-3 and Figure 7-4)? To answer this question, the growth rates at various supersaturations for a solution (Run B-41) containing $1 \times 10^{-7}$ moles PbCl$_2$ per mole KCl are also plotted in Figure 7-3 (Curve D).

This figure shows now that an increase of PbCl$_2$ concentration from about $1 \times 10^{-8}$ to $1 \times 10^{-7}$ moles/mole will move a curve from the position of curve A or B or C to the position of curve D. It appears then likely that variations of the nature of $0.5 \times 10^{-8}$ to $2 \times 10^{-8}$ can account for the difference of the three curves A, B and C. It should be noted that a shift from curve C to B means a shift in the growth rate from 70 µ/hr to dendritic (at 0.16% supersaturation), while from curve C to A means an

* It was found that some crystallites in the reagent contained as high as $1 \times 10^{-5}$ moles PbCl$_2$. (See Section 8.3.5d.) An excess of 0.4 gm of such a high lead concentration crystallites in a one pound reagent KCl could increase the average lead concentration from $1 \times 10^{-8}$ to $2 \times 10^{-8}$ molar ratio.
increase from 30 μ/hr to dendritic (at 0.12% supersaturation).

An attempt to even out variations in composition from run to run was made by mixing a single bottle of thirty pounds of KCl together, from which one pound samples were taken for use to prepare the crystal growth solutions. It was not effective, however, as a comparison of the runs G-23 to G-35, which were all prepared from the same reagent bottle, indicates. (See Table 7-3.)

The findings of this investigation, regarding the incorporation of PbCl₂ in KCl crystals, can provide a reason why the scattering persisted even after the mixing of the big batch: the portion of the initial impurities of the reagent KCl, which will be contained in the saturated solution, are expected to depend strongly on the saturation procedure.

Variation in Impurity Content due to the Saturation Procedure. The saturation procedure appears to be very important in determining the final purity and especially the lead content of the solution. This fact can very well account for the variation in growth rates, since no particular attention was paid during this investigation to the saturation procedure.

It is evident from the results on the incorporation of Pb in KCl crystals (discussed in Chapter 8) that Pb is captured by the precipitating crystals to such an extent
that most of the lead is contained in the crystals crystallized first.

This has the following consequences: If a saturated solution is prepared by mixing water and potassium chloride and then heating it up to saturation temperature, the solution will contain all of the lead of the dissolved KCl. However, if the solution is prepared by heating first to a temperature higher than the saturation and then cooling it to saturation temperature, much of the lead will be included in the precipitated crystals. The amount of PbCl₂ precipitated will depend upon the growth rate (i.e., rate of cooling). In addition, when a solution is saturated for a very long period of time, then small crystals will dissolve and large ones will grow. In this way lead will be extracted from the solution.

It is concluded, therefore, that the impurity content of the crystal growth solutions may vary because of variations a) in the impurity content of the reagent, KCl, used for the preparation of the solution, and b) in the procedure of saturation.

These variations could probably account for the poor reproducibility in the growth rate measurements in different solutions for a given supersaturation.

In Chapter 8 a procedure for the preparation of very pure solutions or crystals of KCl is described. That procedure is recommended to be used in future crystal
growth studies, not only of KCl, but also of other alkali halides as well.

In this investigation the problem of the variation in growth from solution to solution was bypassed, by using the same solution in order to study the effect of a variable—such as the rate of stirring, supersaturation, or radiation dose rate.

c) Effect of Stirring Rate on Growth Rate - Region Where Mass Transfer is the Controlling Rate

Experimental work by Cartier et al (48), on the crystallization of citric acid and itaconic acid, showed that the growth rate increases with increasing solution velocity as one would expect if liquid phase mass transfer is important. However, these investigators have also observed that at sufficiently high velocity, the growth rate becomes independent of the velocity.

A similar behavior was observed for the potassium chloride in this investigation. Inspection of Figure 7-2 shows that at low growth rates, the growth rate was independent of the stirring rate (or the liquid velocity), for stirring rates ranging from 600 to 1200 rpm. At higher growth rates, however, the growth rate increased as the stirring rate increased from 400 to 850 rpm and then became independent of the liquid velocity.

The liquid velocities at the point inside the flask where the crystals were growing, for three different stirring
rates, are presented in Table 7-6. The velocities were measured by a small Pitot tube.

**Table 7-6**

**Liquid Velocities Corresponding to Various Stirring Rates**

<table>
<thead>
<tr>
<th>Stirring Rate rpm</th>
<th>Liquid Velocity fps</th>
<th>cm sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>1.4</td>
<td>43</td>
</tr>
<tr>
<td>900</td>
<td>1.6</td>
<td>49</td>
</tr>
<tr>
<td>1100</td>
<td>2.0</td>
<td>61</td>
</tr>
</tbody>
</table>

It is concluded, therefore, that for 0.12% supersaturation when a stirring rate higher than 850 rpm was employed, the liquid phase mass transport was not the controlling resistance, as long as the crystals were growing at a rate less than about 150 microns per hour. It should be noted that for low growth rates, the minimum stirring rate could be less than 850 rpm.

In all the growth experiments performed in this investigation, at 0.12% supersaturation, stirring rates higher than 850 rpm were employed. Thus, mass transfer through the surrounding liquid was not the controlling rate.

**Theoretical Correlations.** Mass transfer rates can be calculated by using one of the analytical expressions which
have been developed to relate the mass transfer coefficient $K$ to hydrodynamics and diffusional characteristics of the liquid where transfer takes place.

One such semi-empirical equation, developed by Froessling (75) for mass transfer to or from single spheres is the following*:

$$N_{Sh} = 2 + 0.552(N_{Re,S})^{1/2} (N_{Sc})^{1/3} \quad (7-1)$$

where

$N_{Sh} = \text{Sherwood number, } Kd/D_v$

$N_{Re,S} = \text{sphere Reynolds number, } dU_p / \mu$

$N_{Sc} = \text{Schmidt number, } \mu / \rho D_v$

$K = \text{mass transfer coefficient, } \text{cm/sec}$

$D_v = \text{diffusion coefficient, } \text{cm}^2/\text{sec}$

$d = \text{sphere diameter, } \text{cm}$

$\rho = \text{solution density, } \text{gm/cm}^3$

$\mu = \text{solution viscosity, } \text{gm/cm/sec}$

$U = \text{liquid velocity, } \text{cm/sec}$

* The Garner and Suckling equation (78) was also considered. However it gave much higher values than the experimental. (See Appendix A10.)
Values of the mass transfer coefficient, for crystals of KCl, growing at 0.12% supersaturation and 35°C temperature, were calculated using the Froessling equation and from them mass transfer rates. (See Appendix A10.) The calculated mass transfer rates are plotted in Figure 7-5 together with the two experimental curves of Figure 7-2. Although Froessling's equation has been developed for spheres only, the calculated curve is remarkably close to the part of the experimental curve, where the mass transfer is presumably the controlling rate. There is, therefore, close agreement between experimental data and calculated values regarding the region where mass transfer is controlling.

Additional experiments are needed, more specifically at low liquid velocity (down to 1-10 cm/sec) and high supersaturations (conditions which prevail in industrial crystallizers), to establish the extent of applicability of the Froessling equation.

The establishment of an equation predicting growth rates when mass transfer in the liquid is the controlling step is very important; it will provide the limiting rate at which potassium chloride could be deposited on a crystal surface at given flow conditions and supersaturation; that is valuable information for the design of a crystallizer.

d) Morphology of Formed KCl Crystals - Dendritic Growth

Although in the seed crystals only (100) faces were
MASS TRANSFER CONTROLLING

SUPERSATURATION: 0.12 %
- EXPERIMENTAL CURVES
- CURVE CALCULATED THROUGH FROESSLING EQUATION

FIGURE 7-5
MASS TRANSFER CONTROLLING REGION IN KCl CRYSTAL GROWTH WITH NO PbCl₂ ADDED
Additional experiments are needed, more specifically at low liquid velocity (10 cm/sec) and high supersaturation (5000% in industrial crystallizers), to substantiate the extent of applicability of the preceding equations.

Values of the mass transfer coefficients for crystals are calculated from the mass transfer equation (see Appendix A10). The results are presented in Table 7-2 together with a theoretical value calculated for a sphere in a moving fluid. Although in some cases the numerical values are close together, it is generally known that close agreement is not obtained.

Values of the mass transfer coefficients for crystals are calculated from the mass transfer equation (see Appendix A10). The results are presented in Table 7-2 together with a theoretical value calculated for a sphere in a moving fluid. Although in some cases the numerical values are close together, it is generally known that close agreement is not obtained.

Additional experiments are needed, more specifically at low liquid velocity (10 cm/sec) and high supersaturation (5000% in industrial crystallizers), to substantiate the extent of applicability of the preceding equations.

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present, the grown crystals of KCl contained in addition (110) and (111) faces. (See Figure 6-9.) The (110) faces were not well defined; their presence, however, is established by the hexagonal shape of the (111) faces. (See Figure 6-10.)

However, while the faces remained planar at low growth rates, the growth became dendritic at high growth rates. In dendritic growth the face of a crystal becomes very irregular, marked by the appearance of numerous projections on it. (See Figure 7-6.)

It was observed, during this investigation, that the (100) faces were planar for supersaturations giving growth rates up to about 160 μ/hr. When, however, the supersaturation was increased further, dendrites were always formed. This supersaturation level, above which dendritic growth takes place, was varying from solution to solution (compare curves A, B and C in Figure 7-3; see also Figure 7-4.) for the reason explained above in Section 7.1.3b.

For crystallization experiments with a stainless shaft, this supersaturation level was between 0.14% and 0.20%.

The value of the critical growth rate of 160 μ/hr corresponds to 150 layers/second. The magnitude of this critical rate is consistent with a report that sodium chloride crystals are poorly formed at growth rates above
0.07 gm/cm²/hr; that is, 300 layers/sec. (144).

The formation of the above dendrites can be interpreted in the light of the mechanism of dendritic and whisker growth (2,146) as follows:

An inspection of Figure 7-5 shows that for supersaturations about 0.12% and stirring rates below around 1000 rpm (which were the prevailing conditions in the experiments of the present investigation), the liquid phase mass transport resistance becomes important when the growth rate exceeds the value of 160 μ/hr. It can be recalled, however, that this is exactly the critical rate above which dendritic growth occurs. This is not an accidental coincidence. According to the theories of dendritic growth (146), one of the instances when dendritic formation is promoted is when the mass transfer resistance is controlling the rate. Under these conditions a small projection existing on a crystal surface protrudes rapidly into the solution, where it meets a higher concentration of solute and will grow even more rapidly than the rest of the crystals since it is in a more favorable diffusional environment. If many protrusions participate in this process, a dendritic morphology will result.

The question is now, however, how these protrusions are formed in the first place. As pointed out in Chapters 3 and 4, monatomic growth steps originate from a step source on the surface, which could be an active dislocation
group. These could coalesce into larger steps in two ways:
a) by the bunching mechanism described in Section 3.6 and
b) by the action of impurities as follows (see Section 4.1.3): when the rate of step formation is high, the steps will move across a surface, which possesses a low impurity density. This low density is due to the fact that the spacing between steps, and thereby the time elapsed between the passage of two steps, is very small. For this reason the steps will travel fast.

If a step, however, slows down for some reason, the impurity density on the surface ahead of it will keep increasing, causing a further retardation of the step advance. The steps, therefore, which move fast behind the slowed step will soon overtake it, forming a macroscopic step. Since steps are moving from a source toward all directions, a macroscopic terrace could be formed, which could provide the basis for the formation of a dendrite.

Recapitulating, it can be said that the condition favoring formation of dendrites out of small protrusions is the mass transfer to be the controlling rate. For these protrusions however to exist, the right conditions should exist: high rate of step formation, high step velocity and presence of impurities; if the step velocity is slow, not enough steps can overtake the slowed down step to form the macroscopic step, and if on the other hand not enough
impurities are present, the step is not slowed down enough for the other steps to "catch up".

This seems to be the case in run B-39 (Curve A, Figure 7-2). The crystals grown at 400 and 650 rpm stirring rates were grown under conditions at which mass transfer was the controlling rate. However, no dendrites were formed, probably because either the step velocities were low or the impurities were present in a small amount. That the amount of impurities was small is suggested from the fact that in the above run the growth rates were higher than in run A-50 (Curve B, in the same figure), although in both runs the supersaturation was the same.

It should be emphasized that the critical growth rate for dendritic growth is 160 μ/hr only for 0.12% supersaturation. At higher supersaturations, the curve in Figure 7-5, calculated through the Froessling equation, will move upwards to higher values of growth rates, and dendritic growth will start at higher growth rates.

e) Nucleation in the Solution - Secondary Nucleation

Although the objectives of this investigation did not specifically include a study of the nucleation of new crystals in the solution, some observations concerning the appearance of new nuclei were made during the course of this investigation. Since these observations are related to dendritic growth, they will be presented here.

During this investigation, the formation of dendrites
on the seed crystal was always accompanied by the appearance of a large number of new nuclei crystals in the solution. The first explanation could be that dendritic growth took place at relatively high supersaturations, and it is possible that at these supersaturations three-dimensional nucleation - homogeneous or heterogeneous - is favored.

Experiments, however, showed that nucleation occurred only in the presence of one or more seed crystals. More specifically in three occasions a supersaturation of 0.32% was established in the solutions. No nucleation appeared in these solutions even after seven hours. However nucleation of numerous new crystals occurred in less than 15 minutes after the introduction of one seed crystal. The growth on the seed was extremely dendritic. It should be emphasized that the seed crystals never caused nucleation in solutions in which the seed was growing in a regular way (non-dendritic).

It was concluded, therefore, that the nucleation at those conditions was a secondary nucleation. Primary nucleation was observed in supersaturations higher than 0.35%.

Secondary nucleation is the phenomenon in which a crystal, or a primary nucleus, gives birth to a large number of fresh nuclei, which otherwise would not had been formed spontaneously.
This phenomenon was first recognized by Miers in 1911 (quoted in Ref. 121) and has been observed since then in many salts crystallized from aqueous solutions, including KCl (121,125).

Secondary nucleation has puzzled the crystallization investigators, because the secondary nuclei appear to be formed not only in actual contact with the parent crystal, but mostly at some little distance from it.

Recently Powers (140) has considered the origin of the secondary nuclei and examined two possibilities. The first assumes, like Volmer's theory of crystal growth (see Section 3.3.1), the existence of a weakly attracted adsorbed layer of the solute at the crystal surface. The shearing action of the stirred solution may well then be able to draw off part of this layer into the supersaturated environment where it will have the opportunity to grow.

The other possibility is that a crystal can grow dendritically, under certain experimental conditions, and that the fragile dendrite branches are broken off by the shearing action of the solution, and these small particles can then grow in the supersaturated solution. Since it takes a finite time for such a particle to grow to a size observable with the naked eye, the secondary nuclei are first observed in some distance from the parent crystal. Powers (140), working with sucrose, observed secondary
nucleation, while he failed to grow dendrites from sucrose. He concluded then that the first of the above mechanisms is probably responsible for the secondary nucleation.

However, the experimental evidences of this investigation presented above point to the second mechanism, i.e., that dendritic growth is responsible for the secondary nucleation.

Recently Melia and Moffit (124) reached the same conclusion. Under a microscope they actually observed dendritic branches breaking away from an ammonium chloride crystal and growing as secondary nuclei.

It was concluded in the last section that dendritic growth does not occur in the region where the mass transfer of the solute is not the controlling rate. It can, therefore, be concluded that secondary nucleation does not also occur in that region.

Since the number of the secondary nuclei, when formed, is much greater than the number of the primary, knowledge of the conditions which favor secondary nucleation is very important.

f) Effect of Supersaturation on Growth Rates

The curves representing the variation of growth rate with supersaturation (Figure 7-3) for solutions containing no additives are characteristic of crystals growing from solutions containing impurities. Very similar curves have been obtained by Beck (8), for adipic acid in presence of additives.
This is not surprising, however, since the "pure" solutions of potassium chloride were shown above to contain Pb$^{++}$ in a concentration of the order of $10^{-8}$ moles/mole KCl.

For this reason the curves for these solutions will be discussed in Section 7.2.3 together with the curves for solutions to which lead chloride was added.

### 7.2 Growth Rates from Solutions Containing Added PbCl$_2$

#### 7.2.1 General-Previous Data

As it was mentioned in Section 4.1.1, with the exception of the data on the effect of surface active agents on the growth of adipic acid crystals, obtained by Michaels and his coworkers (8), hardly any information is available concerning the effect of additives on absolute growth rates.

This is true also for the effect of PbCl$_2$ on KCl crystals.

Yamamoto (180) and Kading (102) studied the effect of PbCl$_2$ on the habit of KCl. Both observed that PbCl$_2$ caused the appearance of (110) and (111) faces. The (111) face (octahedron) is the predominant face at high concentrations (0.1 mol %) of PbCl$_2$. This indicates only that PbCl$_2$ reduces the relative growth rate of (111) faces with respect to (100); it does not give any information regarding the effect on the (100) face.
Sears (153) observed qualitatively the thickening of tiny interference-colored platelets of KCl under the microscope. He reported that the thickening of the (100) face was slowed down even by 1 ppm PbCl\textsubscript{2} in the solution. However he did not measure the observed reduction.

In this investigation a quantitative study of the effect of PbCl\textsubscript{2} on the growth rate of a (100) face of KCl was undertaken; the variables studied were: the supersaturation, the concentration of the PbCl\textsubscript{2} in the solution, and the stirring rate in the crystallizer.

7.2.2 Results of Present Investigation

a) Growth Rate as a Function of Supersaturation

The growth rates of (100) faces of KCl were determined as a function of supersaturation for various concentrations of PbCl\textsubscript{2} as an additive.

The results for a concentration of $10^{-7}$ moles added PbCl\textsubscript{2} per mole KCl are presented in Table 7-7. Because of the variation in growth rate measurements from solution to solution (to be discussed in Section 7.2.3), only the data obtained by changing the supersaturation in the same solution are considered. A tabulation of growth rate data at various supersaturations obtained from different solutions is included in Appendix A14.

The data of Table 7-7 are plotted in Figure 7-7. It can be observed that the data from runs B-41 and S-16 fit the same curve, but not the data from run G-41.
### Table 7-7
Growth Rates of (100) Faces as a Function of Supersaturation in Solutions Containing $10^{-7}$ Moles Added PbCl$_2$ Per Mole KCl

<table>
<thead>
<tr>
<th>Crystallization Temperature</th>
<th>Supersaturation</th>
<th>Growth Rate $\mu$/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>1. Run B-41 (Saturation Temperature 35.8°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.40°C</td>
<td>0.26 ± 0.01</td>
<td>6 ± 1.2</td>
</tr>
<tr>
<td>35.30</td>
<td>0.32</td>
<td>15.5 ± 5</td>
</tr>
<tr>
<td>35.25</td>
<td>0.35</td>
<td>25 ± 7.5</td>
</tr>
<tr>
<td>35.20</td>
<td>0.39</td>
<td>27 ± 7.5</td>
</tr>
<tr>
<td>35.10</td>
<td>0.45</td>
<td>43 ± 10</td>
</tr>
<tr>
<td>35.00</td>
<td>0.51</td>
<td>Dendritic</td>
</tr>
<tr>
<td>2. Run S-16 (Saturation Temperature 35.0°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34.62</td>
<td>0.38</td>
<td>25 ± 6</td>
</tr>
<tr>
<td>34.49</td>
<td>0.51</td>
<td>99 ± 6</td>
</tr>
<tr>
<td>34.46</td>
<td>0.54</td>
<td>Dendritic</td>
</tr>
<tr>
<td>3. Run G-41 (Saturation Temperature 35.8°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.10</td>
<td>0.44</td>
<td>24 ± 9</td>
</tr>
<tr>
<td>35.00</td>
<td>0.51</td>
<td>36 ± 9</td>
</tr>
<tr>
<td>34.90</td>
<td>0.58</td>
<td>96 ± 9</td>
</tr>
</tbody>
</table>
**FIGURE 7-7**

**GROWTH RATE AS A FUNCTION OF SUPERSATURATION**

---

**PbCl₂ CONCENTRATION: 10⁻⁷ MOLES/MOLE KCl**

Each point represents a different crystal:
- ○ Run B-41
- △ Run S-16
- □ Run G-41

+ shows estimated errors
DENDRITIC GROWTH REGION

PbCl₂ CONCENTRATION: $10^{-6}$ MOLES/MOLE KCl
EACH POINT REPRESENTS A DIFFERENT CRYSTAL

○ RUN G-45
△ ALL OTHER RUNS: (SEE TABLE 7-8)

SHOWS ESTIMATED ERROR
IN GROWTH RATE.
ERROR IN SUPERSATURATION ± 0.01

FIGURE 7-8
GROWTH RATE AS A FUNCTION OF SUPERSATURATION
The results for a concentration of $10^{-6}$ moles PbCl$_2$ per mole KCl are presented in Table 7-8 and plotted in Figure 7-8. Again the data from one of the solutions fit a different curve than the data obtained from the other solutions.

Finally, Table 7-9 presents the results from solutions containing $10^{-5}$ moles PbCl$_2$ per mole KCl. These data are plotted in Figure 7-9 together with the data obtained from solutions containing $10^{-6}$ (Figure 7-8) and $10^{-7}$ (Figure 7-7) moles PbCl$_2$/mole KCl. In the same plot the data from solutions containing about $10^{-8}$ moles PbCl$_2$/mole KCl, that is from "pure" solutions (see Figure 7-3), are included. Thus, Figure 7-9 summarizes the growth rates of KCl as a function of supersaturation, for PbCl$_2$ concentrations ranging from $10^{-8}$ to $10^{-5}$ moles/mole KCl.

b) Effect of Stirring Rate on Growth Rate

The effect of stirring rate on the growth rate from solutions containing added PbCl$_2$ was studied by growing crystals at different stirring rates in the same solution.

The data from three different solutions are presented in Table 7-10 and plotted in Figure 7-10 (Runs B-40 and B-41) and 7-11 (Run B-42).

The stirring rate was varied from 400 rpm up to 1100 rpm. The latter was the maximum stirring rate possible under the conditions of the experiment. At higher stirrer
Table 7-8
Growth Rates of (100) Faces as a Function of Supersaturation in Solutions Containing 10^{-6} Moles PbCl_2 Per Mole KCl

<table>
<thead>
<tr>
<th>Run</th>
<th>Crystallization Temperature</th>
<th>Supersaturation</th>
<th>Growth Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>µ/hr</td>
</tr>
<tr>
<td>G-37</td>
<td>35.0°C</td>
<td>0.64 ± 0.01</td>
<td>5 ± 1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G-39</td>
<td>35.5</td>
<td>0.96</td>
<td>30 ± 9</td>
</tr>
<tr>
<td></td>
<td>35.0</td>
<td>1.28</td>
<td>59 ± 9</td>
</tr>
<tr>
<td>G-40</td>
<td>35.15</td>
<td>0.87</td>
<td>15 ± 3</td>
</tr>
<tr>
<td></td>
<td>35.0</td>
<td>0.96</td>
<td>46 ± 9</td>
</tr>
<tr>
<td></td>
<td>34.85</td>
<td>1.05</td>
<td>45 ± 9</td>
</tr>
<tr>
<td>G-42</td>
<td>35.5</td>
<td>1.28</td>
<td>49 ± 9</td>
</tr>
<tr>
<td></td>
<td>35.15</td>
<td>1.51</td>
<td>106 ± 9</td>
</tr>
<tr>
<td></td>
<td>35.0</td>
<td>1.60</td>
<td>Dendritic</td>
</tr>
<tr>
<td>G-45</td>
<td>35.1</td>
<td>1.41</td>
<td>43 ± 9</td>
</tr>
<tr>
<td></td>
<td>35.0</td>
<td>1.48</td>
<td>52 ± 9</td>
</tr>
<tr>
<td></td>
<td>34.9</td>
<td>1.54</td>
<td>62 ± 9</td>
</tr>
<tr>
<td>B-31</td>
<td>35.15</td>
<td>1.60</td>
<td>126 ± 12.5</td>
</tr>
</tbody>
</table>
Table 7-9
Growth Rates of (100) Faces as a Function of Supersaturation in Solutions Containing $10^{-5}$ Moles PbCl$_2$ Per Mole KCl

<table>
<thead>
<tr>
<th>Run</th>
<th>Crystallization Temperature</th>
<th>Supersaturation %</th>
<th>Growth Rate $\mu$/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-42</td>
<td>35.0</td>
<td>$1.60 \pm 0.01$</td>
<td>$5.0 \pm 1.5$</td>
</tr>
<tr>
<td>G-46</td>
<td>35.0</td>
<td>1.92</td>
<td>$10.0 \pm 3.0$</td>
</tr>
<tr>
<td></td>
<td>34.8</td>
<td>2.04</td>
<td>$10.0 \pm 1.5$</td>
</tr>
<tr>
<td>G-47</td>
<td>35.0</td>
<td>2.24</td>
<td>$16.0 \pm 3.0$</td>
</tr>
<tr>
<td></td>
<td>34.8</td>
<td>2.36</td>
<td>$20.0 \pm 1.5$</td>
</tr>
<tr>
<td>G-48</td>
<td>35.2</td>
<td>2.44</td>
<td>$21.0 \pm 3.0$</td>
</tr>
<tr>
<td></td>
<td>35.0</td>
<td>2.56</td>
<td>$25.0 \pm 4.5$</td>
</tr>
<tr>
<td></td>
<td>34.8</td>
<td>2.68</td>
<td>$30.0 \pm 1.5$</td>
</tr>
<tr>
<td>S-18B</td>
<td>32.75</td>
<td>4.65</td>
<td>Dendritic</td>
</tr>
</tbody>
</table>
Table 7-10
Effect of Stirring Rate on Growth Rate
in Presence of PbCl₂

(PbCl₂ Concentration: 10⁻⁷ Moles/Mole KCl)

<table>
<thead>
<tr>
<th>Run</th>
<th>Super-saturation %</th>
<th>Stirring Rate RPM</th>
<th>Advancement of Basic Plane (100) Faces µ/hr</th>
<th>Over-All Growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-41</td>
<td>0.38</td>
<td>400</td>
<td>27 ± 7.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>27 ± 7.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>27 ± 7.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>29.5 ± 7.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1100</td>
<td>27 ± 7.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1100</td>
<td>25 ± 7.5</td>
<td></td>
</tr>
<tr>
<td>B-40</td>
<td>0.43</td>
<td>400</td>
<td></td>
<td>148 ± 12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td></td>
<td>160 ± 12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650</td>
<td></td>
<td>101 ± 12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650</td>
<td></td>
<td>96 ± 12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>42 ± 10</td>
<td>81.5 ± 12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>44.5 ± 10</td>
<td>89 ± 12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1100</td>
<td>44.5 ± 10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1100</td>
<td>44.5 ± 10</td>
<td></td>
</tr>
<tr>
<td>B-42</td>
<td>0.44</td>
<td>400</td>
<td>42 ± 7.5</td>
<td>101 ± 12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>47 ± 7.5</td>
<td>101 ± 12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650</td>
<td>44.5 ± 7.5</td>
<td>72 ± 12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650</td>
<td>49.5 ± 7.5</td>
<td>81.5 ± 12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>39.5 ± 7.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
<td>44.5 ± 7.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1100</td>
<td>42 ± 7.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1100</td>
<td>44.5 ± 7.5</td>
<td></td>
</tr>
</tbody>
</table>
Figure 7-9

Effect of supersaturation and PbCl₂ concentration on (100) face growth rate.

Concentrations of PbCl₂:
- A, A' 10⁻⁸ moles/mole KCl
- B, B' 10⁻⁷ moles/mole KCl
- C, C' 10⁻⁶ moles/mole KCl
- D, D' 10⁻⁵ moles/mole KCl

Curves A', B', C' were obtained from different solutions than curves A, B, C.

Shows estimated error.
**Figure 7-10**

Effect of stirring rate on growth rate of KCl (PbCl₂ added).

- **PbCl₂ conc.** $10^{-7}$ moles/mole KCl
- **Supersaturation:**
  - △ 0.43%
  - ○ 0.38%
- Shows estimated errors

Points 5 & 5* correspond to measurements of two different kinds of growth on the same crystal (see text section 7.2.3d).
PbCl₂ CONC. 10⁻⁷ MOLES/MOLE KCl
SUPERSATURATION: 0.44%
I SHOWS ESTIMATED ERROR

ALL POINTS FROM THE SAME
SOLUTION (B-42). POINTS 3 & 3*
AND 4 & 4* CORRESPOND TO
MEASUREMENTS OF TWO
DIFFERENT KINDS OF GROWTH
ON THE SAME CRYSTAL
(SEE TEXT SECTION 7.2.3d)

---

**FIGURE 7-II**

EFFECT OF STIRRING ON GROWTH
RATE OF KCl
(PbCl₂ ADDED)
CRYSTAL NO
(See Fig. 7-10)
STIRRING RATE
400 RPM 650 RPM 850 RPM 1100 RPM

DIRECTION OF FLOW

FRONT FACE
SIDE FACE
BACK FACE

FIGURE 7-12
CRYSTALS GROWN AT VARIOUS STIRRING RATES IN THE SAME SOLUTION
PbCl₂ Conc: 10⁻⁷ moles/mole KCl

(Explanation for the Photographs on the Next Page)
speeds, cavitation caused the appearance of numerous bubbles, which interfered with the growth of the seed.

Pictures of four crystals from run B-40 are presented in Figure 7-12.

It was observed in both runs B-40 and B-42 at low stirring rates that clusters of small crystallites were appearing on the crystal faces. (See pictures in Figure 7-12.) This resulted in high growth rates in these crystals. In some cases, when the clusters were not covering the whole surface, the basic planes of the cubic seed could be observed and their advancement to be measured. This is reported in Table 7-10 at the column "advancement of basic plane". In the instances, however, where clusters were developed on the crystal surface, the over-all growth, including the increase in size due to the clusters, was also measured and reported as "over-all growth".

It was also observed that the appearance of the clusters was always accompanied with the appearance of a small number (not more than a hundred) of nuclei inside the solution. The nuclei were definitely much less than the nuclei appearing in the case of dendritic growth.

7.2.3 Discussion of the Results

a) Reproducibility of the Data

The discussion regarding the reproducibility of the growth rate measurements, which was presented in
Section 7.1.3, applies also to the solutions in which PbCl₂ was added. The factors contributing to the error in growth rate measurements in that case (i.e., in "pure" solutions), namely the error in supersaturation determination and the variation in Pb content of the reagent KCl, are important here also.

An additional factor, however, is introduced: the variation in the concentration of the added PbCl₂. The PbCl₂ was added in the following manner: to obtain a solution of 10⁻⁷ moles/mole KCl, one drop of a stock solution (of suitable concentration - see Appendix A3.3 for sample calculations) was added from a burette; for a 10⁻⁶ solution four drops of another solution; and for a 10⁻⁵ solution a weighed amount of PbCl₂. In the last case the error involved would be less than 1%. In the other two cases, however, where drops are involved, the variation in the volume of drop could be as much as 10%.

Inspection of Figure 7-9 shows that, as expected, there is no scattering in the data from solutions containing 10⁻⁵ moles PbCl₂/mole KCl. It is observed, however, that in 10⁻⁶ solutions a considerable difference exists between the curve C' for one of the solutions and the curve C for all the others. The magnitude of the difference is such that it cannot be explained by the above-mentioned factors, which suggests an accidental experimental error, for instance, drying of solution at the
tip of the burette and carrying down of the salt to the
crystallizer by the subsequent drop.

In $10^{-7}$ solutions, however, the difference between
B and $B'$ can be explained; it was shown (see Section 7.1.3)
that the variation in the concentration of PbCl$_2$ in the
reagent KCl is of the order of $10^{-8}$. Such a variation,
combined with the variation in the amount of added PbCl$_2$,
could account for the shifting of curve B to $B'$.

It should be emphasized, however, that these fluctua-
tions in rate measurements from solution to solution did
not affect the present studies of the effect of certain
variables on the growth rate, because every time a variable
was studied, the same solution was used throughout the
experiment.

b) General Effect of PbCl$_2$ on the Growth Rate of KCl

As the concentration of PbCl$_2$ in the solution was
increased from $10^{-8}$ mole fraction to $10^{-5}$, the growth rate
on the (100) faces of KCl decreased. (See Figure 7-9.)

It might be assumed that the growth rate in a truly
pure solution is higher than in solutions containing $10^{-8}$
moles of PbCl$_2$/mole KCl. However this is not necessarily
true.

Beck (8) found that the rate on (100) faces of adipic
acid increases at first as the concentration of an impurity
(surfactant) increases (at any given supersaturation);
then the rate drops drastically to a much lower level at
sufficiently high impurity concentrations.

It would be interesting, therefore, to determine the growth rate of KCl from pure solutions and observe if the growth is enhanced in a similar way at low concentrations of PbCl₂. The technique suggested in Chapter 8 for the production of Pb free solutions could be used.

c) Effect of Supersaturation on Growth Rate

The striking characteristic of the curves in Figure 7-9 (see also Figures 7-3, 7-7, 7-8) is the drastic increase in growth rate (for a given PbCl₂ concentration) when a certain supersaturation is attained.

This behavior could be explained either by the Sears mechanism (152), (see also Section 4.1.3 of present report) in which the additive adsorbs on the advancing steps or by Cabrera-Vermilyea and Frank's mechanism (47,73) in which the adsorption takes place on the planar regions between steps.

It will be concluded in Section 8.3.4 from lead incorporation data that lead is adsorbed not only at the kink sites of the advancing steps, but also on the surface regions between steps; i.e., both the above mechanisms are probably operating.

It was attempted originally, during this investigation, to fit curves calculated from Equation (4-24) in the growth rate data of Figure 7-9. The detailed calculations are included in Garavito’s S.M. thesis (77).
This attempt, however, was not successful; this can be explained, now, by the observation that lead ions do not adsorb only at the kink sites as Equation (4-24) assumes.

The fact that both mechanisms are operating, each to a certain degree, makes difficult the development of an expression which could account quantitatively for the observed dependence of growth rate upon supersaturation and lead concentration (Figure 7-9).

However, the data can be explained qualitatively by invoking the Cabrera-Frank model. It was pointed out in Section 4.1.3 that if their model is correct, a steep increase in the growth rate of a crystal with increasing supersaturation would be expected (at constant concentration of impurities). This is exactly the case with the observed data (Figure 7-9).

As one recalls from the discussion in Section 4.1.3 when the supersaturation increases, the rate of step formation increases and the spacing between steps thereby becomes smaller. For a given step velocity, then, less time is allowed for PbCl₂ to adsorb before the next step passes. The steps would begin to encounter smaller impurity concentrations on the surface, and their rate would increase. This rate increase, however, would allow less time for the lead ions to adsorb, and their concentration on the planar regions between steps would be further reduced. A cascading effect is developed in
this way that can account for the abrupt change in the growth rate for small changes in supersaturation.

A similar cascading effect is expected with increasing lead concentration (for a given supersaturation). At sufficiently high Pb concentrations the propagation of a step is slowed considerably. As a result more time is available for the adsorption of Pb in front of the step. As the Pb concentration increases, the velocity of the step will be reduced further. This cascading effect probably accounts for the drastically increased effectiveness of Pb at high concentrations.

It should be noted, that in order to vary the supersaturation in the same solution, the temperature of crystallization has to be varied. However, all crystal growth theories indicate that the effect of this variable is less significant than the effect of supersaturation, and it can be neglected.

d) Effect of Stirring Rate on Growth Rate

An inspection of Figures 7-10 and 7-11 shows first that at low growth rates (Run B-41 in Figure 7-10), the growth rate is independent of the stirrer speed, at least for the range of 400 to 1100 rpm. At higher growth rates, however, the growth rate is independent of the liquid velocity only for stirring rates higher than about 1000 rpm. When the stirring rate is reduced below 1000 rpm, the "over-all" growth rate starts increasing rapidly.
This is exactly the opposite of what was observed in solutions containing no additives (Figure 7-2). There the growth rate at low stirring rates decreases as the latter decreases. The explanation given there was that the mass transfer of the solute through the liquid phase is the controlling resistance in that region.

The observed increase of growth rate, in solutions containing $10^{-7}$ moles PbCl$_2$/mole KCl at low stirring rates, can be explained in a similar way, if it is assumed that the mass transfer of the lead ions (impurity) through the liquid phase is now the controlling resistance. Roughly speaking, as the liquid velocity decreases, the amount of lead which diffuses to the crystal is reduced, and the retardation of the KCl growth becomes smaller. The mechanism by which this increased growth is created will be discussed in Section (e) below.

This reasoning suggests that under certain experimental conditions the diffusion of the impurities becomes the important factor in crystal growth. It is suspected, therefore, that in the crystallization experiments in presence of additives, which have been reported in the literature and in which slow or no stirring was provided, the diffusion of the impurity was probably the controlling rate. That means that the effect of those impurities on the crystal habit was grossly underestimated.

Generally speaking the role of the impurity diffusion
through the liquid has not been adequately recognized in crystallization processes, in contrast to the recognition given to the role of the solute diffusion.

It is suggested that both processes would be operating in a solution; the combined effect of the two diffusions would give the dependence of growth rate upon stirring rate. This can be represented schematically in Figure 7-13. Curve A represents the effect of the solute diffusion, while B, the effect of the impurity diffusion. The relative magnitude of the two conflicting effects could be either as in plot (a) (low impurity concentration - small retarding effect) or as in (b) (high impurity concentration). In the latter case the combined curve goes through a maximum.

![Diagram showing the combined effect of solute and impurity diffusion on growth rate](image)

**FIGURE 7-13**

SCHEMATIC REPRESENTATION OF THE COMBINED EFFECT OF SOLUTE AND IMPURITY DIFFUSION ON GROWTH RATE
It seems that in solutions containing $10^{-8}$ molar fraction PbCl$_2$ (Figure 7-2), the situation is as in (a), while in solutions containing $10^{-7}$ (Figures 7-10 and 7-11), the situation is as in (b).

No experimental data were found indicating the existence of such a maximum in the effect of stirring rate on the growth rate. This is suggested as a topic of future investigation.

However, a similar behavior has been observed by Mullin and Raven (131,132) in the investigation of the crystal nucleation rate. They found that the nucleation rate for certain salts increases originally with the intensity of agitation, but goes through a maximum and starts decreasing at higher stirring rates.

Their explanation did not involve the diffusion of impurities. However, a more possible explanation can be offered, based on the effect of stirring rate on the diffusion rate of impurities. Their findings, together with the explanations offered by them and by this investigation, are discussed in Appendix A13.

In conclusion, it is suggested that the diffusion rate of impurities is an important factor in crystallization process, and closer attention should be paid to it.

**e) Mechanisms of Formation of Crystal Clusters at Slow Stirring - Boundary Layer Nucleation**

An inspection of the crystal pictures of Figure 7-12
indicates that the crystal becomes more and more irregular as the stirring rate decreases. The irregularity is a result of the appearance of large spherical clusters of crystallites on the crystal surface. A consequence of the cluster formation was also a high "over-all" growth rate (Table 7-10).

In some cases, namely at the stirring rates where clusters were formed but were not enough to cover the whole face (for example crystals grown at 850 rpm in Run B-40 and 650 rpm in Run B-42 - see Figures 7-10 and 7-11), the advancement of the basic plane of the (100) faces could be observed and measured. The growth rate, calculated in that way, was found the same as the growth rate at high stirring rates (1100 rpm). This means that the increased "over-all" growth rate is due exclusively to the formation of the clusters and also that the clusters are formed by a mechanism, which operates simultaneously and independently from the normal mechanism of growth, but overtakes it at very low stirring rates (400 rpm in Figure 7-12).

The normal growth was concluded above (Section 7.2.3b) to be a layer growth process retarded by adsorbed lead ions through the Cabrera-Frank mechanism, but also to some extent through the Sears mechanism. The cluster formation mechanism, on the other hand, is related to a mass transport process in the liquid phase,
since it becomes more important as the stirring rate becomes smaller.

The diffusing species are: the solute and the lead ions (complex or single). It could be said that the diffusion of the solute becomes the controlling rate at low rpm and as a result dendritic growth takes place; this dendritic growth might produce the observed clusters. However, although dendrites are possible at conditions in which solute diffusion is rate-controlling, their growth rate could never exceed the growth rate of the same crystal at higher stirring rates, where bulk diffusion is not the controlling rate. That means that the growth rate of a dendrite on crystal No. 6 (Figure 7-12) could never be greater than the growth rate of crystal No. 4. This is contrary to what was observed experimentally (see Table 7-10). Therefore diffusion of the solute alone cannot account for the formation of the clusters at slow stirring.

The diffusion of lead ions will be considered next. It is shown in Chapters 4 and 8 that a large amount of Pb is adsorbed and subsequently incorporated into the growing crystal of KCl. For instance, the concentration of lead in a crystal, grown at the same conditions as crystal No. 6 in Figure 7-12, is 77 x 10^{-6} moles/mole KCl, while the concentration in the solution is 1 x 10^{-7} moles PbCl₂/mole KCl.
It can be assumed that this large amount can be supplied to the crystal at high stirring rates. However, at slow stirring the diffusion of the lead ions will probably become the controlling rate.

In that case a region will exist in the boundary layer - close to the crystal surface - in which the lead concentration will be extremely low.

It is possible for nucleation to occur in the boundary layer for the following reason: the supersaturation in the solution is such (0.44%) that nucleation would occur, if the lead ions were not present. It can be theorized therefore that nucleation may take place in the region where a very low local concentration of Pb exists, i.e., in the part of the boundary layer which is close to the growing crystal surface. Some of these nuclei could drift towards the solution and grow to independent crystals. It was mentioned earlier (Section 7.2.2b) that such secondary nucleation in the solution does actually accompany the appearance of the clusters on the crystal seed surface.

The nuclei, however, which remain inside the boundary layer, will start growing fast. The faster growth will be in the direction of the least lead concentration, which is towards the crystal surface. There the nuclei could join the growing surface. At the same time the nuclei grow towards the other directions; by so doing, however, a nucleus adsorbs lead and depletes the solution.
around itself. In other words, it creates the conditions which favor the formation of other nuclei. This kind of chain nucleation could lead to the appearance of the observed cluster formations.

It was mentioned in a previous section (Section 7.1.3e) that primary nucleation occurs in a "pure" solution of KCl only if the supersaturation is higher than 0.35%. The question is, "Could the supersaturation close to the surface be as high as 0.35%?"

Using a mass transfer coefficient calculated from the Froesiling equation for 650 rpm, and the mass transfer rate calculated from the growth rate of crystal No. 6 of Figure 7-12, the supersaturation at the interface was calculated. A value of 0.36% was found, which makes the nucleation at that point possible, if the concentration of PbCl₂ does not exceed 10⁻⁸ moles per mole KCl.

It should be noted that the edge of the critical nucleus was calculated to be about 0.7 microns for a 0.36% supersaturation, much lower than the magnitude of the boundary layer thickness.

The above discussed nucleation process, which could be termed boundary layer nucleation, might account also for some cases of secondary nucleation (see discussion in 7.1.3), which are still unexplained (99), even by breaking of the dendritic branches.
7.3 Summary of Chapter 7

a) Crystal growth rate measurements indicated that even "pure" solutions, prepared from reagent grade KCl contained lead in the order of $10^{-8}$ moles/mole KCl.

b) Higher growth rates were obtained in an all-glass crystallizer than in a crystallizer containing stainless steel parts (shaft and crystal holders).

c) The growth rate measurements were reproducible inside the same solution, but different solutions gave widely different results under the same conditions. This was attributed to variations in the purity of the solution.

For this reason the effect of the various variables was studied always inside the same solution.

d) The conditions under which the growth rate is not controlled by diffusional processes in the liquid were determined experimentally. The data were successfully correlated with the Froessling equation.

e) Dendritic growth occurs in the region where mass transfer of the KCl in the liquid phase is the controlling rate.

A mechanism for the formation of dendrites under these conditions was suggested.

f) Secondary nucleation always accompanied the formation of dendrites. The idea that secondary nuclei originate from broken dendritic branches is thus supported.

g) The growth rates of the (100) faces of KCl were
determined as a function of supersaturation for four concentrations of PbCl$_2$: $10^{-8}$, $10^{-7}$, $10^{-6}$ and $10^{-5}$ moles per mole KCl.

Cabrera-Vermilyea and Frank's mechanism was used to explain qualitatively the observed dependence.

h) An increase in the over-all growth was observed in a solution containing $10^{-7}$ moles PbCl$_2$/mole KCl, when the stirring rate was reduced below a critical value.

It is suggested that below this stirring rate the diffusion of PbCl$_2$ in the liquid phase becomes the controlling rate. The amount of PbCl$_2$ reaching the crystal decreases with reduced stirring, and the growth rate consequently increases.

The role of impurity diffusion in the crystallization processes in general was emphasized.

i) A mechanism was proposed to account for the observed formation of crystal clusters at the surface of the KCl crystals at slow stirring: at low stirring rates the boundary layer is depleted of Pb by the growing crystal; thereby, it constitutes a favorable site for the formation of new nuclei.
8.1 Determination of Impurity Content

A number of potassium chloride crystals grown during the present investigation, (see Chapter 6 for growth procedure) were analyzed in order to determine the amount of a certain impurity that they captured from the solution.

The impurities determined were Pb++, Fe++, Ti++, Bi+ and Hg++. The incorporation of Pb++ was the most thoroughly investigated.

8.1.1 The Method of Analysis

The amount of impurities contained in the dry crystals of potassium chloride was determined spectographically. The concentration of the desired element was estimated by comparing the intensity of a certain spectrum line of this element with the same line from a standard which contained a known concentration of the element.

The analyses were performed by Jarrell-Ash Company (Waltham, Massachusetts) by the use of its Mark IV Ebert Spectrograph.

The intensity of the lines of the spectrum was registered on a glass plate coated with a photographic emulsion. Spectra of the various standards and of the unknown were photographed alternately on the same plate and under the same conditions.
The standards were prepared by mixing dry potassium chloride crystal powder (spectographic quality) with a certain amount of an impurity compound (PbO in the case of Pb). The standard with the highest concentration of impurity was prepared first. The others were then prepared by diluting it with potassium chloride.

Finally, a photometric comparison of the intensity of the lines was employed by the use of Jarrel-Ash's comparator microphotometer.

A more detailed description of the method and the procedure is included in Appendix A5.1.

8.1.2 Preparation of the Sample for Analysis

The crystals to be analyzed were weighed in an analytical balance (2 to 6 crystals in each sample, weighing from 20 to 100 milligrams). Each sample was put into a small vial and sent to Jarrell-Ash Company for analysis.

There the crystals of each sample were crushed together in a quartz mortar. Then the powder was put into another vial along with a glass bead. The vial was put on a vibrator for about five minutes, in order for the sample to become homogenized.

A small quantity of the homogenized sample (in most of the cases 5 milligrams) was weighed on the pan of a torsion type precision balance and transferred into a small core in a graphite electrode. A known quantity of an internal standard material was also added and the elec-
trode carrying the sample was ready to be introduced into
the spectrograph (see Appendix A5.1 for the significance
of the internal standard).

The identical procedure was followed for the standard
mixtures, which contained a known concentration of the ele-
ment to be determined.

8.1.3 Calculation of Impurity Concentration in the
Grown Part of the Crystal

The spectrographic analysis gave the average concen-
tration of the impurity into the crystal. The crystals,
however, which were sent for analysis, consisted of two
parts: the seed part and the part which was grown from the
solution on top of the seed. The concentration of the
impurity in the grown crystal part was desired. To deter-
mine this concentration from the average concentration,
the amount of the grown crystal and the impurity concen-
tration in the seed part should be known.

The amount of the grown part was found by subtract-
ing the weight of the seed from the total weight. The
weight of the seed was calculated from its dimensions,
which were measured microscopically. The impurity concen-
tration of the seed was determined by analyzing spectro-
graphically parts of the large melt crystal, from which
the small seeds were cleaved.
8.2 Results

The results from the following two series of impurity determinations are presented:

Series I (Table 8-1)

These determinations were conducted with the purpose of investigating the effect of the following variables on the lead uptake by potassium chloride crystals.

a) concentration of lead in the solution
b) growth rate of the crystal
c) stirring rate

Series II (Table 8-2)

In this series the uptake of other impurities, besides lead, was investigated (i.e. Fe^{+++}, Hg^{++}, Bi^{++} and Ti^{+++}).

The growth experiments and the calculations of Series II were performed by S.A. Sanni (145). The recycling flow apparatus described in Appendix A15.1 was used for these experiments. The stirring rate was 900 rpm., however, the liquid velocity due to the geometry of the flask, was much lower than in the crystallized used for the growth of the Series I crystals: 16 cm/sec as compared to 40-60 cm/sec.
### TABLE 8-1
Lead Content of KCl Crystals

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Run No.</th>
<th>Lead Conc. in Solution (Added) moles/mole KCl</th>
<th>Lead Conc. in crystals mol/mole</th>
<th>Estimated % error</th>
<th>Supersaturation (Δt)**</th>
<th>Stirring Rate rpm</th>
<th>Growth Rate μ/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>G-49</td>
<td>0*</td>
<td>22 x 10^{-6}</td>
<td>± 5.0%</td>
<td>0.2,03°C</td>
<td>1000</td>
<td>Dendritic</td>
</tr>
<tr>
<td>2</td>
<td>G-49</td>
<td>1 x 10^{-9}*</td>
<td>21</td>
<td>2.5%</td>
<td>0.1°C</td>
<td>1000</td>
<td>52 ± 2.5</td>
</tr>
<tr>
<td>3</td>
<td>G-49</td>
<td>1 x 10^{-8}*</td>
<td>27</td>
<td>3.0%</td>
<td>0.1,02°C</td>
<td>1000</td>
<td>95 ± 2.5</td>
</tr>
<tr>
<td>4</td>
<td>B-28</td>
<td>1 x 10^{-6}</td>
<td>200</td>
<td>3.5%</td>
<td>2.5°C</td>
<td>900</td>
<td>52 ± 2.5</td>
</tr>
<tr>
<td>5</td>
<td>B-41</td>
<td>1 x 10^{-7}</td>
<td>168</td>
<td>20%</td>
<td>0.4°C</td>
<td>850</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>6</td>
<td>B-41</td>
<td>1 x 10^{-7}</td>
<td>94</td>
<td>17%</td>
<td>0.5°C</td>
<td>850</td>
<td>15 ± 5</td>
</tr>
<tr>
<td>7</td>
<td>B-41</td>
<td>1 x 10^{-7}</td>
<td>145</td>
<td>17%</td>
<td>0.55°C</td>
<td>850</td>
<td>25 ± 7.5</td>
</tr>
<tr>
<td>8</td>
<td>B-41</td>
<td>1 x 10^{-7}</td>
<td>83</td>
<td>17%</td>
<td>0.6°C</td>
<td>850</td>
<td>27 ± 7.5</td>
</tr>
<tr>
<td>9</td>
<td>B-41</td>
<td>1 x 10^{-7}</td>
<td>165</td>
<td>15%</td>
<td>0.7°C</td>
<td>850</td>
<td>42 ± 7.5</td>
</tr>
<tr>
<td>10</td>
<td>B-41</td>
<td>1 x 10^{-7}</td>
<td>76</td>
<td>9%</td>
<td>0.8°C</td>
<td>850</td>
<td>Dendritic</td>
</tr>
<tr>
<td>11</td>
<td>B-41</td>
<td>1 x 10^{-7}</td>
<td>56</td>
<td>9%</td>
<td>0.7°C</td>
<td>850</td>
<td>101 ± 12.5</td>
</tr>
<tr>
<td>12</td>
<td>B-42</td>
<td>1 x 10^{-7}</td>
<td>78</td>
<td>13%</td>
<td>0.7°C</td>
<td>1100</td>
<td>42 ± 7.5</td>
</tr>
<tr>
<td>13</td>
<td>B-42</td>
<td>1 x 10^{-7}</td>
<td>77</td>
<td>10%</td>
<td>0.7°C</td>
<td>650</td>
<td>76.5 ± 12.5</td>
</tr>
<tr>
<td>14</td>
<td>B-41</td>
<td>1 x 10^{-7}</td>
<td>120</td>
<td>20%</td>
<td>0.6°C</td>
<td>1100</td>
<td>25 ± 7.5</td>
</tr>
<tr>
<td>15</td>
<td>B-41</td>
<td>1 x 10^{-7}</td>
<td>93</td>
<td>20%</td>
<td>0.6°C</td>
<td>400</td>
<td>27 ± 7.5</td>
</tr>
</tbody>
</table>

*Note: Although samples 1, 2 and 3 contain a different concentration of added PbCl₂, the actual concentration in all three was of the same magnitude i.e. 10^{-8} moles/mole KCl (see Section 7.1.3b).

** A Δt = 0.1°C corresponds to 0.063% supersaturation.
<table>
<thead>
<tr>
<th>Run No</th>
<th>Impurity added</th>
<th>Impurity concentration in solution moles/mole</th>
<th>Growth Rate μ/hr</th>
<th>Impurity concentration in crystals 10⁶ moles/mole KC1</th>
<th>Supersaturation Δt</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-16D</td>
<td>Pb⁺⁺</td>
<td>1 x 10⁻⁷</td>
<td>74 ± 37</td>
<td>Pb 130(± 70%)</td>
<td>0.8</td>
</tr>
<tr>
<td>S-16F</td>
<td>Pb⁺⁺</td>
<td>1 x 10⁻⁶</td>
<td>99 ± 37</td>
<td>Fe 200(± 40%)</td>
<td>2.4</td>
</tr>
<tr>
<td>S-16H</td>
<td>Pb⁺⁺</td>
<td>1 x 10⁻⁵</td>
<td>27 ± 37</td>
<td>B1 333(± 40%)</td>
<td>3.4</td>
</tr>
<tr>
<td>S-3A</td>
<td>Fe³⁺⁺</td>
<td>1 x 10⁻⁶</td>
<td>25 ± 10</td>
<td>Hg N.D.</td>
<td>0.35</td>
</tr>
<tr>
<td>S-15D</td>
<td>Bi³⁺⁺</td>
<td>1 x 10⁻⁷</td>
<td>111 ± 37</td>
<td>N.D. (&lt;4.3)</td>
<td>0.40</td>
</tr>
<tr>
<td>S-15G</td>
<td>Bi³⁺⁺</td>
<td>1 x 10⁻⁶</td>
<td>122 ± 37</td>
<td>N.D. (&lt;4.3)</td>
<td>0.50</td>
</tr>
<tr>
<td>S-15K</td>
<td>Bi³⁺⁺</td>
<td>1 x 10⁻⁵</td>
<td>148 ± 37</td>
<td>N.D. (&lt;29)</td>
<td>0.3</td>
</tr>
<tr>
<td>S-9</td>
<td>Hg⁺⁺</td>
<td>1 x 10⁻⁷</td>
<td>198 ± 74</td>
<td>N.D. (&lt;100)</td>
<td>0.35</td>
</tr>
<tr>
<td>S-10</td>
<td>Hg⁺⁺</td>
<td>1 x 10⁻⁶</td>
<td>165 ± 50</td>
<td>N.D. (&lt;24)</td>
<td>0.45</td>
</tr>
<tr>
<td>S-11A</td>
<td>Hg⁺⁺</td>
<td>1 x 10⁻⁵</td>
<td>138 ± 37</td>
<td>N.D. (&lt;42)</td>
<td>0.25</td>
</tr>
<tr>
<td>S-12D</td>
<td>Ti⁺⁺⁺</td>
<td>1 x 10⁻⁶</td>
<td>74 ± 37</td>
<td>N.D. (&lt;8.6)</td>
<td>0.25</td>
</tr>
<tr>
<td>S-12F</td>
<td>Ti⁺⁺⁺</td>
<td>1 x 10⁻⁵</td>
<td>99 ± 37</td>
<td>N.D. (&lt;90)</td>
<td>0.25</td>
</tr>
</tbody>
</table>

*N.D. = not detected
8.3 Discussion of Results

8.3.1 Validity of Results

The following four quantities are used in the calculation of the impurity concentration in the grown part of the crystal: the total weight of the sample, the weight of the grown crystal part, the impurity concentration of the seed part, and the average impurity concentration of the whole crystal sample.

a) Error in obtaining the total weight

The samples were weighed in an analytical balance. Usually the weight was around 20 milligrams. Therefore, the relative (percentage) error was less than 1%.

b) Error in obtaining the weight of the grown part

The weight of the seed was calculated from its dimensions, which were measured microscopically. The precision of the final figure was also of the order of 1%.

However, the weight of the grown part, which was obtained by subtracting the crystal seed weight from the total weight, may be uncertain by over 20%. This loss in accuracy is due to the small weight of the grown part, obtained as the difference between two large numbers.

Only the contribution of the error in the weight of the grown part, as well as of the error in the total weight, to the overall error is presented in Tables 8-1 and 8-2 (as "estimated percentage error"). The contribution of the remaining two factors, namely the impurity con-
tent of the crystal seed and the experimental error of the analytical method, proved to be difficult to express quantitatively.

c) Impurity content of the crystal seed

Crystal seeds were obtained by cleaving large crystals (10-20 gms) grown from melt. Parts taken from this large crystal were also analyzed spectrographically.

The results of this analysis are discussed in detail in Appendix A5.2. It is concluded there that the impurity content varies from point to point in the large melt crystal. This introduces an uncertainty in the calculation of the impurity concentration in the grown part of the crystal; this uncertainty cannot be estimated quantitatively. It is shown, however, in Appendix A5.2 that this uncertainty is not so large as to affect the magnitude at least of the final value of impurity concentration, or to impede the study of trends in impurity uptake.

d) Reliability of the spectrographic method of analysis

The spectrographic method is considered accurate and precise for the determination of lead or iron, especially for concentrations higher than 10 ppm.

To check the precision of the method two or three determinations were performed from the same homogenized sample. The results are presented and discussed in Appendix A5.3. The average percentage deviation was for both, Pb and Fe, around 11.5%.
8.3.2 Uptake of Pb by KCl Crystals

a) Crystal lead concentration as a function of the solution lead concentration

The data presented in Tables 8-1 and 8-2 indicate that the concentration of lead in the KCl crystal ranged from $21 \times 10^{-6}$ moles/mole KCl for the most dilute solutions up to $280 \times 10^{-6}$ for the solution of $10^{-5}$ moles PbCl$_2$/mole KCl. There is a scattering in the values of the crystal lead concentration for each solution lead concentration. For instance in a solution concentration of $1 \times 10^{-7}$ moles Pb/mole KCl it varies from 56 up to 168 depending on the growth rate of the crystal. Nevertheless there is a definite qualitative trend indicating that the crystal lead concentration increases with an increase in lead content of the solution. For instance, if the average crystal lead concentration is plotted as a function of the solution concentration, the curve of Figure 8-1 is obtained. This curve has only qualitative value; although it resembles an adsorption isotherm, it is not a true adsorption isotherm, because as it will be emphasized below the lead adsorbed on the crystal surface does not always attain equilibrium with the lead in the solution.

The same curve indicates that the concentration of Pb in the crystal approaches a saturation value. This value, however, appears to be at least one order of magnitude lower than the maximum value of $6 \times 10^{-3}$ moles PbCl$_2$/mole
FIGURE 8-1
CONCENTRATION OF LEAD IN CRYSTALS vs
CONCENTRATION IN SOLUTION
KCl reported by Hahn (85). Hahn produced the crystals from a potassium chloride solution saturated with lead chloride. Therefore, it is possible that, by evaporating, the solution became supersaturated not only in respect to potassium chloride but also to lead chloride. This then might have caused an oriented overgrowth of PbCl$_2$ on KCl. These small crystallites might have been included consequently inside the KCl crystal, resulting in the reported high lead concentration. Booth (18) observed the formation of oriented overgrowths of PbCl$_2$ on the (100) faces of NaCl, when the crystal was covered with a drop of saturated solution of PbCl$_2$.

The value of the saturation concentration itself, however, is of no great practical significance. What is important is the variation of the value of the lead distribution coefficient (i.e. the ratio of the lead concentration in the crystal to the concentration in the solution) as a function of the lead concentration in the solution.

There is a definite qualitative trend in the data indicating that the distribution coefficient decreases with an increase in lead content of the solution. This is, obviously, a consequence of the fact that the concentration of lead in the crystal approaches a saturation value as the solution concentration increases. In Table 8-3 the average distribution coefficients for each lead concentration are presented.
TABLE 8-3
Average Distribution Coefficients of Pb in KCl

<table>
<thead>
<tr>
<th>Concentration of PbCl₂ in solution</th>
<th>Average concentration of Pb in crystals</th>
<th>Average distribution coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>moles/mole KCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$1 \times 10^{-8}$</td>
<td>$23 \times 10^{-6}$</td>
<td>2300</td>
</tr>
<tr>
<td>$1 \times 10^{-7}$</td>
<td>$105 \times 10^{-6}$</td>
<td>1050</td>
</tr>
<tr>
<td>$1 \times 10^{-6}$</td>
<td>$200 \times 10^{-6}$</td>
<td>200</td>
</tr>
<tr>
<td>$1 \times 10^{-5}$</td>
<td>$280 \times 10^{-6}$</td>
<td>28</td>
</tr>
</tbody>
</table>

The distribution coefficient becomes as low as 28 when the solution concentration is increased to $1 \times 10^{-5}$. Some qualitative experiments by Yamamoto (180) indicated that the coefficient finally becomes smaller than unity. (see also Figure 4-7) The solution lead concentration at which this happens (about $10^{-3}$ moles PbCl₂/mole KCl) is very significant. It is the concentration of lead in a crystal which cannot be reduced effectively by repeated recrystallization. This point will be discussed further in Section 8.3.5, where the practical consequences of this phenomenon are presented.

It can be seen in Table 8-1 (sample no. 3) that in this investigation distribution coefficients as high as 2700 were found. Käding, however, working with ThB (which is an isotope of Pb) found (102) its distribution coefficient in KCl to be 57; this coefficient was also quite independent
of the experimental conditions and the impurity concentration in the solution for concentrations up to $10^{-4}$ moles PbCl$_2$/mole KCl. This discrepancy, however, can be explained if the conditions of the crystal growth experiments are compared.

Käding produced his KCl crystals either by slowly evaporating or slowly cooling a saturated solution without any stirring. It was pointed out above in Section 7.2.3d that at low stirring rates the mass transfer of Pb$^{++}$ in the liquid may become the controlling rate. Therefore, in Käding's experiments where no stirring was provided the amount of Pb adsorbed was the minimum. In addition the solution lead concentration was not constant during each run. Thereby he actually reported an average value of the distribution coefficient over the concentration range he worked with (initial concentration about $10^{-4}$ moles Pb/mole KCl). This also results in low values for the distribution coefficient.

In this investigation, on the contrary, vigorous stirring of the solution was used and the crystals grew under conditions of constant impurity concentration.

It was pointed out above that for a given solution lead concentration, the crystal lead concentration (and the distribution coefficient) varied with the growth rate of the crystal. This dependence will be discussed next.
b) Variation of the crystal lead concentration with the crystal growth rate

It can be recalled, from the discussion in Section 4-2, that the variation of impurity concentration of the crystal with the growth rate has the form of the curve (1) in Figure (8-2), (see also Figure 4-3). The curve will have this form considering either Hall's relation (Equation 4-30) or Chernov's theory (50). It can be seen from this curve, that the impurity concentration in the crystal varies monotonically with growth rate from a value equal to the equilibrium impurity concentration, \( C_o \), to a value virtually identical with the surface concentration of the impurity, \( C_s \) (it is assumed that \( C_o \ll C_s \)).

It was also indicated in Section 4-2 that according to Chernov (50) the criterion which can be used in order to decide whether a growing crystal has a lead concentration close to \( C_o \) or to \( C_s \) is the growth rate value, \( R \), compared to the ratio \( \frac{D_{Pb^{++}}}{h} \)

where \( D_{Pb^{++}} \) = the diffusion coefficient of lead ions in the crystal

\[ h \] = the thickness of the deposited layer

\[ R \] = the growth rate of the crystal

In case \( \frac{D_{Pb^{++}}}{h} \gg R \), the lead concentration in the crystal will have a value close to an equilibrium value, but when \( \frac{D_{Pb^{++}}}{h} \ll R \), then the crystal will have the same lead concentration as on the surface.

In the growth experiments of the present investigation \( D_{Pb^{++}} \) was calculated to be \( 3.8 \times 10^{-19} \text{ cm}^2 \text{ sec}^{-1} \).
FIGURE 8-2
VARIATION OF IMPURITY CONCENTRATION IN THE CRYSTAL WITH GROWTH RATE

(1) HALL'S THEORY ONLY
(2) VARIATION OF SURFACE IMPURITY CONCENTRATION WITH GROWTH RATE
(3) COMBINATION OF BOTH EFFECTS
The value was found by extrapolating the findings of Glasner et al. (81) to 35°C which was the temperature of the crystal growth. The choice of this value is discussed in Appendix A7.

The thickness of a newly deposited layer cannot be estimated easily. Observation of crystals of alkali halides grown under the microscope has shown that they grow by layers spreading across the faces. These layers were several hundred angstrom thick (40). It appears that one of the effects of PbCl₂ is to decrease this thickness. Sears (153) found that when the concentration of PbCl₂ in the solution is 1 ppm, the growth layers appear to be 25 Å thick. (A monatomic layer is 3 Å thick). For the discussed experiments, in which the PbCl₂ concentration was of the order of 0.1 ppm, the layer probably was thicker. The value of 25 Å can be used however. It will become evident that even if a monatomic layer is assumed, the derived conclusion does not change.

Thus \( D_{\text{Pb}^{2+}}/h = \frac{3.8 \times 10^{-19}}{25 \times 10^{-8}} = 1.52 \times 10^{-12} \text{ cm}^2 \text{ sec}^{-1} \). The slowest growth rate, on the other hand, which was observed, was \( R = 6 \mu \text{ hr} \) or \( R = 1.7 \times 10^{-7} \text{ cm/sec} \).

Therefore under the most optimistic conditions, the diffusion rate was almost five orders of magnitude lower than the growth rate. Thus, according to Hall-Chernov model, the plateau in curve 1 (Figure 8-2) has been reached under the conditions of the growth experiments of this
investigation. It would be expected, thereby, the lead concentration in the crystal to be constant and independent of the growth rate.

The present investigation, however, points to the contrary. The concentration of Pb$^{++}$ in crystals as a function of the growth rate of the (100) face is plotted in Figure 8-3, for constant concentration of lead in the solution: $1 \times 10^{-7}$ moles/mole KCl. In spite of considerable scattering (due probably to the variation in the lead content of the seed crystal), there is undoubtedly a decrease in the lead content as the growth rate increases. (The growth rate was increased by raising the level of supersaturation; in some cases, however, by simply decreasing the stirring rate). Hall-Chernov model does not account for such a variation. Therefore, an extension or modification of this model is necessary.

c) Extension of the Hall-Chernov model

One can recall from the discussion in Section 4.2.3 that the assumption behind Hall-Chernov's treatment was that the impurity concentration at the surface, $C_s$ is always constant; i.e. adsorption of the impurity at the crystal surface attains equilibrium.

This assumption, however, is not necessarily true. Actually Frank, in his theory about the effect of impurities on crystal growth (see Section 4.1.3), assumed that the concentration of impurities on the crystal surface is
**Pb**⁺⁺ CONC. IN SOLN 10⁻⁷ moles/mole KCl FOR CRYSTALLIZATION

CONDITIONS, SEE TABLE 8-1

SHOWS ESTIMATED ERRORS

FIGURE 8-3

CONCENTRATION OF Pb**⁺⁺ IN CRYSTALS vs GROWTH RATE OF (100) FACES
time dependent. In other words, in most of the crystal growth cases, the time that elapses between the deposition of successive layers is of the same order of magnitude or smaller than the time required to establish an equilibrium concentration of impurities. Thus, the concentration of impurities at a point on the crystal face does not attain the equilibrium value; it is actually, an increasing function of the time elapsed since the passage of the previous layer. This time is inversely proportional to the growth rate. (More specifically, this time is equal to $y_0/v_\infty$, where $y_0$ the distance between two successive steps and $v_\infty$ the velocity of a step. The growth rate, $R = \frac{av_\infty}{y_0}$, hence the time $\propto 1/R$). This relationship can be expressed graphically by curve 2 in Figure 8-2.

Frank's notion, about the time-dependency of the impurity concentration at the crystal surface, has been used successfully in explaining certain features of crystal growth; for instance, the development of macroscopic growth steps on the crystal surface (73), the formation of whiskers (8), and the dendritic growth (Section 7.1.3d of present investigation). It seems, therefore, that this is a realistic assumption and it could be used, also in the explanation of the impurity incorporation data of the present investigation.

Assuming, therefore, that in the case of PbCl$_2$ in KCl crystals, the adsorption of the lead ion is time dependent,
the two conflicting curves in Figure 8-2 can be combined to give curve (3).

This curve expresses now the dependence of impurity concentration in the bulk of the crystal upon the growth rate. In contrast, to the original Hall-Chernov model, this curve has a maximum. As a result, there are two cases where the impurity concentration would become very small. First at very low growth rates, where the impurity, captured in non-equilibrium concentrations, has time to diffuse towards the surface and leave behind the low equilibrium concentration; secondly, at very high growth rates where the surface does not have time to be covered with impurities.

Hall (86), in his experiments with Sb in Ge crystallized from melt, was working at such conditions (high temperature melting point of Ge: 958.5°C) that the diffusion constant was high enough to make $D_{\text{Sb}}/h \gg R$. In this way he was working under conditions prevailing on the left side of curve 3 (Figure 8-2), and thus found that the impurity concentration increases as the growth rate increases.

In the present investigation, as it was shown above, it is $D_{\text{Pb}^{++}}/h \ll R$. Therefore, the experiments correspond to the region on the right side of the above curve, where the impurity concentration decreases as the growth rate increases.
The question may be asked: under what experimental conditions would the impurity concentration - growth rate dependence indicated by the left side of curve 3 (Figure 2) be observed in the present system of Pb⁺⁺ in potassium chloride crystals? This could happen when the ratio $D_{\text{Pb}^+}/h$ becomes of the same order of magnitude or smaller than $R$.

There are two ways for the ratio $D_{\text{Pb}^+}/h$ and the growth rate $R$ to become of the same magnitude: either by reducing $R$, or by increasing the temperature of the experiment and consequently the magnitude of $D_{\text{Pb}^+}$.

Since $D_{\text{Pb}^+}/h = 1.52 \times 10^{-12} \text{ cm/sec at } 35^\circ \text{C}$ the growth rate should be reduced to this value. In order to observe an increase in the size of the crystal, the crystal should grow at least $25 \mu$. The crystal should be left therefore to grow for about

$$\frac{25 \times 10^{-4}}{1.52 \times 10^{-12} \times 3600} = 4.52 \times 10^5 \text{ hrs}$$

which is an extremely long time.

On the other hand, if the desired growth rate is kept at $1 \mu/\text{hr}$ in order for the ratio $D_{\text{Pb}^+}/h$ to become equal to $1 \mu/\text{hr}$, $D_{\text{Pb}^+}$ should be about $7 \times 10^{-15} \text{ cm}^2/\text{sec}$. This is found to correspond to about $150^\circ \text{C}$. Obviously, this condition is also practically unattainable for aqueous solutions at atmospheric pressures. Therefore if an
experimental reproduction of the whole curve 3 (Figure 8-2) is desired another system should be found.

One way of increasing $D_{\text{Pb}^{++}}$ without increasing the temperature is discussed in Chapter 10. It is suggested there that gamma-irradiation creates enough vacancies to increase the diffusion coefficient of a foreign atom in the lattice several orders of magnitude.

Another question to be answered regards the shape of curve 2 (Figure 8-2), which expresses the concentration of the adsorbed impurity at the surface as a function of the growth rate.

If a Langmuir type isotherm is assumed, then the rate at which the adsorption equilibrium is reached is given by the following equation (114).

$$\frac{N_0 \theta'}{N} \frac{d\theta'}{dt} = a\mu - (v_1 + a\mu)\theta'$$  \quad (8-1)

where $N = \text{the Avogadro constant}$

$N_0 = \text{the number of elementary spaces per unit surface}$

$\mu = \text{number of gram molecules striking the unit surface per unit time}$

$a = \text{the fraction of the striking molecules, that condense}$

$v_1 = \text{the rate at which the gas would evaporate if the surface were completely covered}$

$\theta' = \text{the instantaneous value of } \theta_1$

$\theta_1 = \text{the fraction of the surface covered at equilibrium}$
Integration of (8-1) gives

\[ t = \frac{N_0}{N(1+\alpha \mu)} \ln \frac{\theta_1}{\theta_1 - \theta} \]  

(8-2)

For a given constant concentration of impurity in the solution

\[ t = A \ln \frac{1}{1-e^{\theta_1/\theta}} \]  

(8-3)

where \( A \) is a constant.

Time \( t \) is the time the surface of the growing crystal remains exposed to the solution and depends obviously on the growth rate.

\[ t = \frac{B}{R} \]  

(8-4)

On the other hand, \( \theta' / \theta_1 \) is proportional to the surface concentration of the impurity \( C_s \). Therefore, Equation (8-3) becomes

\[ \frac{B}{R} = A \ln \frac{1}{1-mC_s} \]  

(8-5)

or

\[ C_s = \frac{1 - \exp(-B'/R)}{m} \]  

(8-6)

where \( B' \) and \( m \) are constants.

Equation (8-6) gives us an idea about the shape of curve 2 in Figure 8-2.

It should be emphasized that, like the original Hall-Chernov model, the extended model, which is presented here,
should not be limited to a particular impurity-crystal system. It is reasonable to assume that any impurity, which has the property of adsorbing in a large amount on a crystal face will behave according to the above suggested model.

d) Effect of stirring rate on the impurity incorporation

In the previous section the effect of growth rate on the impurity incorporation was discussed. Growth rate, however, in the experiments discussed above was a dependent variable; it depended upon the supersaturation and the stirring rate (in this investigation the crystallization temperature was not a variable).

To isolate experimentally the effect of stirring rate the supersaturation should be kept constant and the stirring be decreased until the mass transfer of the lead ions in the liquid becomes the rate controlling step.

Points A, B and C in Figure 8-3 satisfy these conditions. The supersaturation is the same in all three cases (0.44% - See samples No. 13, 14, 15 in Table 8-2); the stirring rate varies, being correspondingly 1100, 650 and 400 rpm; and finally the crystals corresponding to 650 and 400 rpm were grown under conditions, where the lead mass transfer rate in the liquid was important (see Figure 7-11).

The correspondence between stirring rate and lead uptake for the three points A, B and C is the following:
Point in Stirring | Pb Concentration | Distr. Coefficients
--- | --- | ---
Fig. 8-3 | Rate | 78± 10 moles/mole KCl | 780
A | 1100 rpm | 77± 8 | 770
B | 650 | 56± 5 | 560
C

The trend is therefore for the crystal lead concentration and the effective distribution coefficient to decrease as the stirring rate decreases. As it was pointed above, this appears to be one of the reasons why Kåding (102) has observed such a low distribution coefficient (= 57) in unstirred solutions.

e) Recapitulation

In summary, the following model was suggested for the incorporation of lead in KCl: At very slow growth rates the concentration of lead in the crystal approaches some equilibrium value \( C_o \), which is constant for the particular crystal-impurity system. \( C_o \) values for the \( \text{Pb}^{++} \)-KCl system are not known. It was assumed, however, to be smaller than the surface impurity concentration \( C_s^0 \). This in turn is larger than liquid bulk equilibrium value \( C_L \); i.e., \( C_o < C_s^0 > C_L \). As the crystal grows and the surface layers are covered by subsequent layers, the lead is incorporated at concentrations \( C_s^0 \) and the net concentration in the crystal bulk exceeds \( C_o \). This sets up a diffusion gradient inside the crystal which tends to decrease the crystal lead concentration towards \( C_o \). When, however, the diffusion rate is extremely small (as in the present experimen-
tal conditions), the net lead concentration in the crystal bulk remains practically equal to $C_s^0$. Thereby, the lead concentration profile in a (100) face of a KCl crystal will look as follows:

![Diagram of concentration profile](attachment:image.png)

The surface impurity concentration does not necessarily have the equilibrium value $C_s^0$. Most probably it has a value $C_s < C_s^0$; this value depends on the time a crystal surface remains exposed to the solution. Thereby the fas-
After the crystal grows the smaller it will be. This is exactly what the experimental data of the present investigation indicated.

The assumption made above that the crystal bulk lead concentration is smaller than $C_s^0$ could be checked in a future study by a theoretical calculation of the solubility of $\text{Pb}^{++}$ in the KCl crystal lattice.

8.3.3 Uptake of Other Impurities by KCl

There is no reason to assume that lead in alkali halides is the only case of non-equilibrium impurity incorporation, i.e. $k_{\text{eff}} > 1$. Actually, as it has been mentioned in Section 4.2.4, besides the case of lead in alkali halides (of the sodium chloride type lattice), the case of lead and ThX (Rd) in alkali sulfates, and cadmium in sodium chloride have been reported in the literature. It is reasonable to assume that any impurity, which has the property of adsorbing in a large amount on a crystal face (i.e. the surface concentration $C_s$ larger than the solution concentration) will behave according to the above suggested model.

The present investigation studied the incorporation of other impurities, besides lead, in potassium chloride crystals, namely of $\text{Fe}^{+++}$, $\text{Tl}^{+++}$, $\text{Bi}^{+++}$ and $\text{Hg}^{++}$. (See Table 8-2)

Each one of the above was added in the solution from which the potassium chloride was crystallized at concentrations ranging from $1 \times 10^{-7}$ moles/mole KCl up to $1 \times 10^{-5}$. 
Iron and titanium were found to behave like lead.

(It should be noted however that only one sample of Ti was analyzed.)

The potassium chloride reagent ("Baker analyzed") which was used for the preparation of the solutions contained about 0.00005% iron. The solution therefore contained ~0.6 x 10^{-6} moles Fe/mole KCl which is of about the same order of magnitude as the concentration of the added Fe^{+++}. It is expected therefore the concentration of Fe in all the grown crystals to be of the same order of magnitude.

Actually, as an inspection of Table 8-2 shows, in two of the samples iron concentration was almost the same, about 300 moles/mole KCl, which corresponds to an effective distribution coefficient of 300. However the third sample more specifically in the crystals growing from the solution, containing bismuth, k_{eff} for iron was about 900. An explanation for this high value cannot be offered at the present time. (see Appendix A12)

No mercury was detected in any crystal sample. The limit of detection was 10 ppm. This means that the distribution coefficient should be less than 4.

Also no bismuth was detected. Since the limit of detection was 0.5 ppm, in this case, it can be said that k_{eff} < 1. (See also Figure 4-6)

It can be concluded, therefore, that from the tested impurities only Fe^{+++} and Ti^{+++} showed a k_{eff} larger than unity.
The question, however, which needs to be answered is not only in what impurity-crystal system the effective distribution coefficient, $k_{\text{eff}}$, is larger than unity but also what properties of the impurity or the lattice determine if the particular impurity is strongly adsorbed and subsequently incorporated into the growing crystal.

This is suggested as the subject for future investigations. Such a study should be combined with growth rate measurements in the presence of impurities, since both incorporation of an impurity and its effect on growth rate can be attributed to adsorption on the crystal surface.

The question arises, could one predict the amount of impurity incorporated from its effect on the growth rate or the crystal habit? What the experimental data indicate with respect to this question will be discussed in the next section.

8.3.4 Relation Between the Incorporation of Impurities and their Effect on the Growth Rate of the Crystal

Lead ions provide an example of impurity which is incorporated inside a crystal and at the same time has a strong effect on the growth rate of the crystal.

The results of the investigation on the effect of lead chloride on the rate of (100) faces of KCl are presented in Chapter 7. It is reported there that PbCl$_2$ retards appreciably the growth rate on that face. No growth rate measurements were conducted for the other faces,
i.e. (110) and (111).

The studies of other investigators (102, 180) however, on the effect of PbCl$_2$ on the crystal habit of KCl indicated that PbCl$_2$ caused the appearance of the (111) faces (octahedral), presumably by reducing the relative growth rate of these faces compared to the (100) faces. Hence, the growth rate of the (111) faces is also retarded by the PbCl$_2$.

Booth (12) has found that in NaCl lead is incorporated along the (100) planes but not along the (111) (see also Section 4.2.4). It will be assumed that the behavior of lead in KCl is the same, since the effect of lead on the habit of KCl and NaCl is similar in both salts (180). Therefore, lead retards the growth on the (111) faces of the KCl, without being incorporated.

It was pointed out in Section 4.1.3 that Sears suggested a mechanism by which mobile impurities can retard the growth on a crystal face. According to it, mobile impurities are adsorbed at the kinks of a monomolecular layer and block its advancement without necessarily being incorporated into the crystal. This mechanism may then be operating on the (111) faces. Since, however, the ionic arrangement on a (111) face and in a kink of a growing (100) face are the same (compare site A with kink B in Figure 8-4) Sears mechanism would also act on the (100) faces.
The incorporation, however, of lead along only the (100) faces indicates that another mechanism is operating in the (100) faces in addition to the possible Sears mechanism. This could be Cabrera-Vermilyea and Frank's
mechanism, also discussed in Section 4.1.3. According to this mechanism an immobile complex may be formed by the adsorption of the lead ions on the planar surface regions between steps. The steps while advancing incorporate these immobile impurities into the crystal.

It is concluded, therefore, that lead ions retard the growth on the (100) faces probably by both, Cabrera et al, and Sears mechanisms and on the (111) by Sears mechanism only. Lead is incorporated however only along the (100) faces.

Besides lead on (111) faces, bismuth also provides an example of impurity, which retards growth without being included. Booth (18) has found that bismuth modifies the habit of sodium chloride, by causing the appearance of (111) faces. This means that bismuth retards the growth at least on the (111) faces of sodium chloride. Yamamoto reports (180) that bismuth modifies the habit of potassium chloride; in addition it was found during this investigation (see Appendix A15.2) that bismuth retards the growth on the (100) faces of potassium chloride. In no case, however, bismuth was incorporated in the crystal in detectable amount (18), see also Table 8-2). It can be assumed then, that the effect of bismuth ions on growth rates follows the Sears mechanism.

Mercuric ions reduce also the growth of the (100) faces of potassium chloride (see Appendix A15.2). The
sensitivity, however, of the mercury determination was such that no conclusion could be attained regarding the incorporation in the crystal (Table 8-2).

Ferric ions are captured in large amounts by the growing KCl crystals (see Table 8-2); the concentration of Fe in a crystal grown from a solution containing $10^{-6}$ moles Fe/mole KCl is even higher than the concentration of Pb in a crystal grown from a solution containing $10^{-6}$ moles Pb/mole KCl. Nevertheless ferric ions have little or no effect on the growth rate in contrast to lead ions. (see discussion in Appendix A12).

In recapitulating, the following can be said about the relation between growth retardation on a crystal plane by an impurity and incorporation of the impurity into the crystal.

a) There are cases where an additive retards the growth considerably but it is not incorporated: Pb$^{++}$ and Bi$^{+++}$ on (111) faces of NaCl and KCl, and Bi$^{+++}$ on (100) faces (Sears mechanism of growth in presence of additives)

b) There are cases where the additive is inhibiting growth and at the same time is incorporated into the crystal: Pb$^{++}$ on (100) faces of NaCl and KCl (Cabrera et al. mechanism) and

c) There are cases where the additive is not or is slightly inhibiting growth nevertheless is considerably in-
corporated into the crystal: Fe$^{+++}$ on (100) faces of KCl.

One cannot, then, predict the effect of an impurity upon the growth from incorporation data and vice versa.

However, the example of Pb in KCl indicated that if one has both, absolute growth measurements and incorporation data of an impurity he may deduce which mechanism of growth is operating in the presence of that impurity.

8.3.5 Engineering Consequences

References to the phenomenon of non-equilibrium capture of impurities (in other words to the fact that in certain cases the impurity distribution coefficient is larger than unity) in the extensive literature on crystallization from solution are very rare. It is obvious, therefore, that its importance in relation to the crystallization process has not been adequately recognized.

The important practical consequences of the phenomenon for the recrystallization and purification processes will be discussed in this section.

a) Limits in the purification by recrystallization

Let it be assumed that the impurity adsorbed on a crystal face follows a Langmuir type isotherm; then the fraction of the impurity adsorbed on the surface, and consequently the fraction of the impurity incorporated into the crystal, will become smaller as the concentration of the impurity in the solution will increase. In other words a large effective distribution coefficient will decrease
continuously and finally will become smaller than one. This is evident for the incorporation of Pb in KCl from the results of this investigation (Table 8-3) as well as from Yamamoto's observations (180). The solution concentration at which $k_{\text{eff}}$ becomes greater than one is of great practical significance. It is the average impurity concentration which cannot be reduced effectively by repeated recrystallization. Actually when $k_{\text{eff}} > 1$, recrystallization does not remove the lead but, as it will be shown below, concentrates it strongly in the first fractions.

b) Variation of impurity incorporation with crystal habit

An impurity ion may adsorb greatly on a certain crystallographic plane, while it may not adsorb at all on a different plane of the same crystal. A characteristic example is lead in sodium chloride crystals. It is adsorbed and incorporated to greater extent on the (100) faces than on the (111) faces (see Section 4.2.4).

This means that if the conditions of crystallization are such that the crystal grows only along crystallographic planes on which the impurity does not adsorb, then a rather pure crystal may be obtained. The crystal habit may be changed, by changing the supersaturation or the temperature of crystallization or mainly by the addition of another additive. This additive, should of course, change the habit without being incorporated itself in the crystal. By
changing the habit, it affects the uptake of a second impurity; depending on whether that impurity adsorbs more or less on the new planes the crystal will be richer or poorer in that impurity.

c) Impurity distribution in crystals during crystallization

A crystal may present a non-homogeneous distribution of impurity since the latter could be incorporated selectively along only certain crystallographic planes.

At the same time when the effective impurity distribution coefficient is very large, the concentration of the impurity in the crystal is at a maximum at the beginning of the crystallization; it is possible that the crystal layers formed later will be successively poorer in the impurity, corresponding to the progressive exhaustion of the solution with respect to the impurity. This is another possible source of inhomogeneous distribution of the impurity inside a crystal.

When a large number of crystals are formed, the impurity for the same reason, may be concentrated strongly in the first fractions.

The distribution of lead in the various fractions of crystallized potassium chloride will be presented as an example. Using the distribution coefficients obtained in this investigation (Table 8-3) the fraction of PbCl₂ precipitated as a function of the fraction of KCl crystallized can be calculated. In Figure 8-5 the fraction of PbCl₂
INITIAL CONCENTRATION OF PbCl$_2$ = $10^{-6}$ MOLES/MOLE KCl

FIGURE 8-5
AMOUNT OF PbCl$_2$ REMAINING IN SOLUTION vs AMOUNT OF KCl CRYSTALLIZED
remaining in solution vs the fraction of KCl crystallized is presented, when the initial lead concentration in the solution is $1 \times 10^{-6}$ moles/mole KCl.

The curve shows an extremely strong separation of lead in the first fractions. For instance, if potassium chloride containing lead chloride is recrystallized, then 90% of the original lead will be precipitated with the first 0.6% of the KCl; the 99.9% of the lead will be contained in the first 1.25% of the crystallized KCl.

Since the first crystals contain most of the lead, those which crystallize later will be of higher purity than the original KCl.

There are two important practical consequences; first that in the reagent grade crystals which have been purified by simple recrystallizations, the distribution of the persistent impurities among the various crystallites should be extremely inhomogeneous; secondly, preparation of very pure potassium or sodium chloride crystals can be achieved through the rejection of the first crystallizing fractions.

d) Distribution of Pb and Fe in reagent grade KCl

"Baker analyzed" reagent KCl is purified by recrystallization. It has been reported to have an average concentration of 0.00005% Fe. It has been found to contain about $3 \times 10^{-6}$% Pb (see Section 7.1.3). It is expected, however, these two impurities to be inhomogeneously distributed among the various crystallites, since for both $k_{eff} > 1$. 

-312-
This hypothesis was confirmed experimentally. Various samples of the above reagent, taken from four different one-pound bottles were analyzed spectrographically. The results are presented in Table 8-4. It can be seen that in the three bottles there were crystallites having an impurity concentration higher than the average. As it is expected, the samples containing less lead also contained less iron.

e) Production of very pure KCl and NaCl

The problem of production of very pure alkali halides has long been recognized.

In spectrography, for instance, there is a need for chemicals (used for the preparation of standards) which should have extremely low concentrations of impurities (below the limit of detection). In addition, since very small amounts are used in the spectrographic analysis (about 5 mg), there should not be parts of crystals or crystallites, containing an impurity in a concentration higher than the average.

It is obvious, from the previous discussion, that NaCl or KCl suitable for spectrography cannot be produced by repeated recrystallization of the chlorides. This is presumably the reason, an indirect method is used; they are produced from the corresponding carbonates by the action of HCl.
TABLE 8-4
Spectrographic Determination of Pb and Fe in "Baker Analyzed" KCl

<table>
<thead>
<tr>
<th></th>
<th>Technique*</th>
<th>Pb ppm</th>
<th>Fe ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bottle 1</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 1</td>
<td>1</td>
<td>~30, ~2, ~1</td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>1</td>
<td>~5, &lt;0.1, &lt;0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~1, &lt;0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>~2, ~1</td>
<td></td>
</tr>
<tr>
<td>Sample 3</td>
<td>2</td>
<td>~30</td>
<td></td>
</tr>
<tr>
<td>Sample 4</td>
<td>2</td>
<td>~4</td>
<td></td>
</tr>
<tr>
<td>Sample 5</td>
<td>2</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td><strong>Bottle 2</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 1</td>
<td>1</td>
<td>&lt;0.1, &lt;0.1</td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>2</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>Sample 3</td>
<td>2</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>Sample 4</td>
<td>2</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td><strong>Bottle 3</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 1</td>
<td>1</td>
<td>1, 2, 0.5</td>
<td>12, 14.5, 11</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1</td>
<td>4, 2.5, 5</td>
<td>44, 29, 35</td>
</tr>
<tr>
<td><strong>Bottle 4</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 1</td>
<td>1</td>
<td>3, 4, 2.5</td>
<td>31, 45, 29</td>
</tr>
</tbody>
</table>

*Technique 1: a quantity of 2-3 gms was crushed and mixed; samples of 5 mg. each were taken for analysis.

Technique 2: a small crystallite of about 5 mg was put directly on the graphite electrode.
The investigators, concerned with the production of large crystals of alkali halides from melt, used in various physical measurements, have complained about the purity of the available "pure" raw material. They have been melting the purest reagent-grade material, still, however, the material contained impurities in harmful levels.

Egli and Johnson (63) emphasize that "there is no commercial source for such a common substance as NaCl that will produce satisfactory crystals for many physical measurements. Certain brands of table salt have proved to be better than the best material from chemical reagent companies, but all of it contains enough lead and various other ions to have a measurable effect on impurity-sensitive properties, such as luminescence."

It is evident from the above remarks that the recrystallization of common salt to produce reagent grade NaCl cannot free it from the Pb$^{++}$ and other ions.

Duerig and Markham (61) dealt also with the problem of obtaining pure large crystals of alkali halides, suitable for studying the effect of high energy radiation on them. They analyzed several alkali halides crystals grown from melt by various chemical companies and found considerable variations of the impurity content in samples of the same alkali halide obtained from any one company. They attributed this to the variation of impurity content of the raw material (reagent grade) used for the prepara-
tion of the melt, and emphasized the need for an exception-
ally pure raw material.

The difficulty in obtaining such very pure alkali halides by recrystallization from solution, is due to the fact that the phenomenon of non-equilibrium capture of certain impurities (i.e. very large distribution coefficient) has probably not been recognized.

When, however, this phenomenon is taken into consideration, certain suggestions with respect to the crystallization technique can be made.

Generally speaking, to get rid of an impurity having a large effective distribution coefficient, the first fractions of the recrystallized material should be collected separately. The subsequent fractions, will be much more pure than the original material. For instance, if KCl containing 1 ppm PbCl₂ is recrystallized, the first 2% of the precipitated KCl should be collected separately. The subsequent fraction should then contain less than 0.001 ppm PbCl₂; i.e. the potassium chloride crystals thus obtained have a PbCl₂ concentration lower at about three orders of magnitude than that of the original crystals.

The fraction of the crystallizing species, which should be precipitated in order to carry down the major part of the impurity, will depend on the nature of the impurity and of the host crystal.

A graph similar to that of Figure 8-5 should be constructed for each case.
Instead of precipitating part of the crystallizing species, sometimes it may be more advantageous to add to the supersaturated solution, before nucleation takes place, seeds from outside and leave them crystallize incorporating the impurities. The advantage is that the same material could be used to adsorb an impurity from many batches.

To have an impurity with large distribution coefficient presents certain merits over an impurity with $k_{\text{eff}} < 1$. In the former case, after the first fractions are filtered out, the mother liquor could be evaporized almost to dryness, recovering this way almost all the recrystallized material.

In practice, however, the situation is not always so simple. Impurities with $k_{\text{eff}} \gg 1$ coexist in the solution with impurities having $k_{\text{eff}} < 1$. In addition, as it was discussed previously, the presence of one impurity may affect - reduce or increase - the distribution coefficient of a second impurity.

The above suggested technique of recrystallization will be very effective in the cases, where it has been proven that the impurity follows the Hall-Chernov mechanism of non-equilibrium incorporation. Such cases are, Pb$^{++}$, Fe$^{+++}$ and Ti$^{+++}$ in KCl, Pb$^{++}$ and Cd$^{++}$ in NaCl, Pb$^{++}$ in KBr, RbCl, SrSO$_4$ and finally Pb$^{++}$ and Rd$^{++}$ in alkali sulfates.

It is suspected, however, that probably Hall-Chernov mechanism is involved in most of the cases of persistent
impurities. Further investigation in this direction will be very fruitful. It is evident from Hahn's (85) and Booth's (18) investigation (see also Section 4.2 of this report) that radioactive isotopes provide a very powerful tool in the study of impurity distribution coefficients, between a solution and a crystal.
CHAPTER 9
RESULTS AND DISCUSSION

DISLOCATION DENSITIES OF KCl CRYSTALS
GROWN WITH AND WITHOUT IRRADIATION

9.1 General

It can be recalled from the discussion in Chapter 5 that Co$^{60}$ gamma rays can produce point defects (vacancies and interstitials) in an alkali halide crystal. Formation of dislocations (line imperfections) by gamma-rays in dry crystals is not predicted by the existing theory.

The mechanism, however, proposed by Seitz (157) to explain the formation of the point defects by the photons (see Section 5.3.2) predicts a dislocation climb (an increase in the length of a dislocation loop - see Section 3.4.4) without changing the existing dislocation density. Crawford and Young (53) were unable to observe such a dislocation climb in dry NaCl crystals irradiated with gamma-rays.

In alkali halide crystals, irradiated while grown from a solution, the situation may, however, be different. In this case the interaction between the point defects (produced by the radiation) and the dislocations may take place at the moment the dislocation is formed or while the dislocation has still a very small length. Thus at high concentrations of point defects, a dislocation may
not simply climb but "climb out", resulting in a lower dislocation density.

To check this point, a small number of KCl crystals grown during this investigation were etched in order to determine their dislocation density. The dislocation density in crystals grown under irradiation was compared with the density in crystals grown without irradiation. A knowledge of the effect of gamma-irradiation on the dislocation density of a KCl crystal should be useful in interpreting the effect of the irradiation on the growth rate of the same crystal. (See Chapter 10.)

The etching process is based on the property of an etching solution to attack a crystal surface preferentially at the points where dislocation lines emerge; an etch pit (of inverted pyramidal form for the cubic KCl crystals) is formed at these points. The formation of the etch pits is explained in more detail in Appendix A4.

Counting the number of pits in a certain area, one can calculate the dislocation density of a crystal surface. Both screw and edge dislocations are revealed by the etching process.

9.2 Experimental Procedure

This part of the investigation involved: a) the development of an etching technique for potassium chloride crystals, and b) the determination of the dislocation
density in the grown crystals of potassium chloride through the use of the etching technique.

9.2.1 Procedure for Etching

Many different etching solutions were screened, and it was found that methanol saturated with ammonium chloride was the most promising one.

In brief the crystals were etched by immersing them into the NH$_4$Cl-saturated methanol for thirty seconds. The temperature of the methanol solution was adjusted to be between 26 and 30 degrees centigrade. The crystals were rinsed by dipping them into anhydrous butyl alcohol. (See Appendix A4 for details of the etching technique.)

9.2.2 Procedure for Dislocation Density Measurement

The grown crystals were cleaved in two halves lengthwise. (See Figure 9-1.) Two cleaved surfaces were produced in this way. Usually only one of the surfaces was etched. Occasionally, however, in order to check the reproducibility of the etching technique, both surfaces were etched and analyzed for mirror image correspondence between etch pits.

Each cleaved surface consisted of two parts: the part belonging to the original seed crystal and the grown part, which surrounds the former. (See Figure 9-1.) The length of the seed was from 1.5 to 2 mm, while the width of the strip belonging to the grown part varied from 0.1 to 0.2 mm.
FIGURE 9-1
CLEAVAGE OF A GROWN CRYSTAL
The density of pits was determined in both parts, the seed and the grown part, at 1000-fold magnification by the use of a ruled grid in the eyepiece of the microscope. The grid consisted of a hundred small squares. Ten squares were picked randomly (by the use of a random numbers table), and the etch pits contained in these areas were counted.

Selection of the Area for the Measurement of Etch Pit Density in the Grown Crystal. The etch pit density was measured in areas belonging to the outer half of the grown region of the crystal for the following reasons: (a) the separating line between seed and grown part was known from growth rate measurements only within an accuracy of ± 0.01 mm, and (b) the dislocation density of the grown part close to the separating line was found to be affected by the adjacent seed part. Dislocation lines, which terminated at the surface of the seed and which belonged to closed loops before the cleaving, may have propagated and closed inside the grown part. This would result in a higher dislocation density in the grown part close to the separating line than in regions more removed from the seed crystal.

Although it would be interesting to study the dislocation density in this "transition" region and the effect on this density of the dislocation density of the substrate, this investigation was confined to measuring the number
of dislocations formed by the growth process of the crystal and not those propagated from the seed. For this reason areas belonging to the outer half of the grown crystal strip (see Figure 9-1) were selected for the etch pit measurement.

Not all the area of the cleaved and etched surface was suitable for pit density measurements. For instance, one third of the area belonging to the grown part of the crystal was usually destroyed by the blade used for the cleaving. Another part contained steps or striations, developed during the cleaving, so that only half (or sometimes less) of the area belonging to the grown part was suitable for pit density measurement.

This area was first inspected under the microscope to determine the uniformity of its pit density. If the density were uniform throughout the whole area, the density was measured in one place. If, however, the density was not uniform, the area was divided in regions (usually two to three regions), each one having a uniform density. The pit density in each region was measured then and recorded.

The ease with which differences in dislocation densities could be recognized visually is demonstrated in Figure 9-2. Four pictures of areas with varying pit density are presented. It can be seen that an area having a dislocation density of $0.95 \times 10^7$ disl./cm$^2$ can be
Picture No. 1
0.95 x 10^7 dislocations/cm²

Picture No. 2
0.65 x 10^7 dislocations/cm²

Picture No. 3
3.5 x 10^7 dislocations/cm²

Picture No. 4
1.5 x 10^7 dislocations/cm²
FIGURE 9-3
COMPARISON OF MATCHED CLEAVAGE FACES
(MIRROR IMAGES)
distinguished very easily from an area of $0.65 \times 10^7 \text{disl./cm}^2$. The same is true for an area of $3.5 \times 10^7 \text{disl./cm}^2$ in comparison with one of $1.5 \times 10^7 \text{disl./cm}^2$, as well as for an area of $0.95 \times 10^7 \text{disl./cm}^2$ in comparison with one of $1.5 \times 10^7 \text{disl./cm}^2$. (Compare the "empty" areas in Picture No. 1 with those in Picture No. 4 - actually the right half of Picture No. 4, which is on focus.)

The important density range, for the discussion in Section 9.4, is from $0.5$ to $1.5 \times 10^7 \text{disl./cm}^2$. It can be concluded that for this range a difference in the density of $0.3 \times 10^7 \text{disl./cm}^2$ can be easily detected by visual observation. Thus, if a uniform dislocation density of $1.5 \times 10^7 \text{disl./cm}^2$ is reported for a crystal, there was no region in that crystal containing less than $1.2 \times 10^7 \text{disl./cm}^2$.

9.3 Results

The detailed data for each etched crystal separately are presented in Appendix A4.3. A summary of the pertinent data will be presented here.

9.3.1 Reproducibility of the Data

Two characteristic examples of mirror image correspondence between etch pits are presented in Figure 9.3.
9.3.2 Dislocation Densities

The dislocation densities were determined in crystals taken from the following four sets of experimental conditions:

a) No PbCl₂ added in the solution.
   No irradiation.

b) No PbCl₂ added in the solution.
   Irradiation (2400 rad/min).

c) $10^{-7}$ moles PbCl₂/mole KCl added.
   No irradiation.

d) $10^{-7}$ moles PbCl₂/mole KCl added.
   Irradiation (2400 rad/min).

The results are presented in Table 9-1. In Figure 9-4 the dislocation density of the grown part is plotted versus the corresponding dislocation density of the adjacent seed crystal part.

9.4 Discussion of the Results

9.4.1 Reproducibility of Etching

In both cases in Figure 9-3, a satisfactory mirror image correspondence between the two cleaved surfaces can be observed. This indicates that the employed etching technique gives reproducible etch pit patterns. (See also Appendix A4.)
### Table 9-1

Dislocation Densities in KCl Crystals

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Crystal No.</th>
<th>Concentration of Added PbCl$_2$ Moles/Mole KCl</th>
<th>Irradiation Dose Rate Rads/Min</th>
<th>Dislocation Density $\text{cm}^2$</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>In Grown Part*</td>
</tr>
<tr>
<td>A-37</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>$1.4 \times 10^7$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2.2</td>
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<td></td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2.6</td>
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<td>A-39</td>
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<td>0</td>
<td>1.5</td>
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<td>3.5</td>
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<td>A-40</td>
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<td></td>
<td>2.8</td>
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<td></td>
<td></td>
<td>0.5</td>
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<tr>
<td>B-21</td>
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<td>$1 \times 10^{-7}$</td>
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<td></td>
<td>3</td>
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<td>2400</td>
<td>2.4</td>
</tr>
<tr>
<td>B-24</td>
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<td>0</td>
<td>2.7</td>
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<td>2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.6</td>
</tr>
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* See text for explanation of why more than one value is given for each crystal.
FIGURE 9-4
DISLOCATION DENSITIES IN THE GROWN PART OF A CRYSTAL vs DISLOCATION DENSITY OF THE SEED

<table>
<thead>
<tr>
<th>ADDED PbCl₂ moles/mole KCl</th>
<th>IRRADIATION rads/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>2400</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>2400</td>
</tr>
</tbody>
</table>
9.4.2. Dislocation Densities in Seed and Grown Parts of the Crystals

It is concluded from the data presented in Figure 9-4 that, in general, the dislocation densities of the crystals grown from solution do not differ greatly from the seed crystals, which had been obtained from melt. In the case, however, of solutions containing $10^{-7}$ moles PbCl$_2$/mole KCl, a slight increase in dislocation density was noted, while in the case of crystals grown under irradiation without PbCl$_2$ addition, a small decrease was observed.

In absolute values the dislocation density of KCl crystals grown without irradiation, as well as crystals grown under irradiation but after PbCl$_2$ addition, lay consistently between $1.4 \times 10^7$ and $3 \times 10^7$/cm$^2$. When, however, the crystals were grown under irradiation with no PbCl$_2$ added in the solution, the dislocation density was mainly found to be between $0.5 \times 10^7$ and $1.1 \times 10^7$/cm$^2$; for two crystals grown under these conditions, the dislocation density was beyond this range, giving values of $2.8 \times 10^7$/cm$^2$ and $2.3 \times 10^7$/cm$^2$. However the region of the crystal which showed the value of $2.8 \times 10^7$ cm$^{-2}$ was representing only 5 per cent of the whole area of the grown crystal part, and when the value was $2.3 \times 10^7$ cm$^{-2}$, the high density may have resulted from the large density of dislocations at the adjacent part of the seed. (See Table 9-1.) This argument is supported by the fact that as the crystal grew
(see Figure 9-5), the effect of the dislocations from the seed diminished, and the dislocation density approached a value of $1 \times 10^7$ dislocations/cm$^2$.

In conclusion, crystals grown without added PbCl$_2$, but under irradiation, contained in the major portion of their volume from $0.5$ to $1.1 \times 10^{-7}$ disl./cm$^2$. However, KCl crystals grown without irradiation in no case contained less than $1.4 \times 10^7$ dislocations/cm$^2$. A similar reduction in the value of the dislocation density under irradiation was not observed when the solution contained $10^{-7}$ moles PbCl$_2$/mole KCl.

Figure 9-6 shows how the etch pit pattern in a crystal containing the reduced dislocation density appears under the microscope (Picture No. 11). The other three pictures represent the cases where no reduction in the dislocation density is occurring.

The above conclusion was confirmed qualitatively by etching four more crystals, in addition to the ten presented in Table 9-1. These crystals were grown from a solution in which no PbCl$_2$ was added: two of them under irradiation (crystals No. B-16-1 and B-18-3 and two without irradiation (B-18-2 and A-28-1). It was observed qualitatively that in both irradiated crystals the distribution of etch pits resembled Picture No. 11 (Figure 9-6), while in non-irradiated crystals resembled Picture No. 10.
FIGURE 9-5
ETCH PIT PATTERN IN CRYSTAL GROWN UNDER IRRADIATION (NO PbCl₂ ADDED)
FIGURE 9-6
ETCH PIT PATTERN IN GROWN CRYSTALS

A: Border between seed and grown region (calculated from the growth rate measurements, accuracy $\pm 10\mu$)

Picture numbers refer to Table A4-2

<table>
<thead>
<tr>
<th>LEGEND</th>
<th>Picture No.</th>
<th>PbCl$_2$ added</th>
<th>Irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>moles/mole</td>
<td>KCl</td>
<td>rad/min</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>0</td>
<td>2400</td>
</tr>
<tr>
<td>12</td>
<td>$10^{-7}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>$10^{-7}$</td>
<td>0</td>
<td>2400</td>
</tr>
</tbody>
</table>
The following sections discuss possible reasons for the apparent effect of $\gamma$-irradiation on decreasing the dislocation density in crystals grown without added PbCl$_2$ and lack of such effect when PbCl$_2$ has been added.

9.4.3 Reduction of Dislocation Density by $\gamma$-Irradiation

The lower dislocation density in crystals grown under irradiation can be attributed to one of the following two mechanisms:

a) Under $\gamma$-irradiation less dislocations are formed. In other words irradiation somehow retards the mechanism which is responsible for the formation of dislocations in crystals growing from solutions, or

b) The same number of dislocations are formed under irradiation as without irradiation, but a fraction of them "climbs out" subsequently.

Each possibility will be discussed separately.

a) Effect of $\gamma$-Irradiation on Dislocation-Forming Mechanism

The origin of dislocations in crystal grown from solution is as yet rather obscure. The most probable mechanism is their introduction by impurities ($2,71$). Cabrera ($47$) suggested such a mechanism, which is discussed in Section 4.1.3. He assumed that a region having a greater than average impurity content may develop in a growing crystal. A bunching of steps appears behind that
region (see Figure 4-1). This bunching will reach a certain height, and then it will likely override the anchored piece of step, leaving behind a dislocation full of impurities.

There is an evidence (presented in Appendix A6) that such impurity "pockets" exist probably in the crystals grown during this investigation.

There is a possibility that $\gamma$-irradiation would retard the formation of dislocations by affecting these high impurity-concentration regions on the surface. Such an effect, however, should also affect the motion of the growth steps and thereby the growth rate. It was found during this investigation that gamma radiation (at least at dose rates of $2400 \text{ rad/min}$) did not affect the growth rate from solutions of $10^{-8}$ moles PbCl$_2$/mole KCl (see Figure 10-1). It seems improbable that gamma-irradiation would affect the mechanism of dislocation formation suggested by Cabrera without also affecting the rate of crystal growth.

**b) Dislocation Climb Under $\gamma$-Irradiation**

In order for a dislocation to "climb out" (see Section 3.4.4), diffusion of vacancies to the dislocation should take place. The dislocation planes in a KCl crystal contain both positive potassium ions and negative chlorine ions ($2,3^1$). Thus, for a dislocation to climb
both positive ion and negative ion vacancies should be absorbed by the dislocation plane.

Positive ion vacancies are available in the crystal as charge compensating vacancies for the incorporated metal ion impurities (i.e., Pb\(^{++}\) and Fe\(^{+++}\)).

Negative ion vacancies are created by the gamma-rays. It was pointed out in Chapter 5 that such a formation is deduced by the appearance of F-color centers, which are actually chlorine ion vacancies, having trapped an electron. The number of vacancies produced is always in excess of those accountable by the momentum transfer directly to the atoms from the energetic electrons.

The various mechanisms proposed to explain this phenomenon were discussed in Section 5.3.2.

One of them, namely Seitz's mechanisms, suggests "evaporation" of vacancies from the dislocation jogs; this obviously leads to negative climb (see Section 3.4.4), which is opposite of what was observed in this investigation (positive climb - "climb out").

The other mechanisms are based on the ionization of Cl\(^-\) to Cl\(^0\) or Cl\(^+\), which then migrate to an interstitial position.

The magnitude of the concentration of both the positive ion vacancies (due to the impurities) and the negative ion vacancies (created by the irradiation) can be estimated. The number of KCl molecules per cm\(^3\) is
1.61 x 10^{22}. The concentration of PbCl\textsubscript{2} for crystals grown from a solution containing 10^{-8} moles PbCl\textsubscript{2}/mole KCl is about 2 x 10^{-5} moles PbCl\textsubscript{2}/mole KCl. Therefore the concentration of Pb in the crystals is 1.61 x 10^{22} x 2 x 10^{-5} = 3.2 x 10^{17} atoms Pb/cm\textsuperscript{3}. There are also at least an equal number of positive ion vacancies, i.e., 3.2 x 10^{17} vacancies/cm\textsuperscript{3}.

The number of negative ion vacancies produced by the gamma-radiation dose rate, employed in this investigation, was found to be about 1 x 10^{15}/cm\textsuperscript{3}/min. (See Appendix A9.1.) In a KCl crystal, growing with a rate of 100 microns/hr, the total number of displacements produced, when the (100) face has advanced 200 microns (which is the case for the etched crystals) is 1.2 x 10^{15} per 1 cm\textsuperscript{2} of crystal surface. (See Appendix A9.2.) The number of positive vacancies in the same volume is 3.2 x 10^{17} x 2 x 10^{-2} = 6.4 x 10^{15}. That means that the number of vacancy pairs in that volume is 1.2 x 10^{15}.

The number of dislocations which have disappeared from the same volume of the crystal is 3 x(2.2 - 0.7) x 10^7 cm\textsuperscript{-2} x 2 x 10^{-2} cm\textsuperscript{2} = 9 x 10^5. (Average dislocation density without irradiation 2.2 x 10^7, and with irradiation 0.7 x 10^7/cm\textsuperscript{2}. The factor 3 is used, because the etching reveals the dislocation lines which are parallel to the one of the three directions of the cubic crystal.)
The number of vacancies corresponding to each one of
the disappeared dislocations is

\[ 2 \times 1.2 \times 10^{15} \]
\[ \frac{1.2}{9 \times 10^5} = 2.7 \times 10^9 \]

This number indicates that the climb of dislocations
by absorption of vacancies is not impossible, especially
when one considers that a dislocation in a growing crystal
could interact with these vacancies, while it is still
close to the surface, and the length of the extra plane
is comparatively small.

The elementary processes involved in the formation
of the vacancies will be discussed next.

**c) Mechanism of Vacancy Formation**

There is not sufficient information to decide
which actually of the processes discussed in Section 5.3.2
takes place during the irradiation of the KCl crystals
grown from a solution of \(10^{-8}\) moles PbCl\(_2\)/mole KCl (i.e.,
crystals containing \(2 \times 10^{-5}\) moles PbCl\(_2\)/mole KCl). One
complication arises from the presence of other impurities:
it has been found (present investigation, Table 8-2) that
the grown crystals contain Fe\(^{+++}\) in a concentration of
about \(3 \times 10^{-4}\) moles/mole KCl, in addition to Pb\(^{++}\).

One tentative scheme, however, could be suggested
based on Varley's mechanism (see Section 5.3.2b): a Cl\(^-\)
loses electrons by the irradiation with photons and becomes positively charged. This positive ion finds itself in an unstable position and moves to an interstitial site. There it will capture ultimately enough electrons to be neutralized. The remaining electron is trapped by the Cl\(^-\) vacancy to form an F-center.

In the experiments of this investigation, the irradiation of the growing crystals was done partially under light.* A portion of the F-centers could have been thus "bleached"; i.e., the electron could have left the trap and reacted with the complex \([\text{Pb}^{++} + \text{positive ion vacancy}]\), reducing the Pb\(^{++}\) to Pb\(^+\) and freeing the positive ion vacancy. The F-center could probably react directly with the Pb\(^{++}\). In any case, the over-all reaction would be

\[
\text{Cl}^- + \left[\text{Pb}^{++} + \Box\right] \rightarrow (\text{Cl in interstitial site}) + \text{Pb}^+ + \Box + \Box^- \tag{9-3}
\]

(The symbol \(\Box\) indicates a vacancy.) The two vacancies formed are those absorbed by the dislocations. According to Schulman (148), the Pb\(^+\) may be reduced further to metallic lead.

* A quartz type infrared heater was used on the on-off regulator to control the temperature of the bath. This heater was emitting light also in the visual spectrum.
The following experiments may be helpful in checking the above suggested mechanism or generally in providing evidences about the actual mechanism.

a) To repeat the growth experiments under irradiation with solution containing a much lower level of impurities and especially Pb\textsuperscript{++}. (See Section 8.4 for the preparation of such a solution.) In that case the number of positive ion vacancies originally present in the crystal will be much smaller. If these vacancies actually contribute to the dislocation climb, the irradiation will not be as effective now in reducing the number of dislocations.

b) To conduct the growth experiments under irradiation in the dark. In that case "bleaching" of the F-centers would not take place, and

c) To obtain the absorption spectra of the crystal. This will tell whether the impurity ions have been reduced or not; for instance, the presence of Pb\textsuperscript{+}, or Pb\textsuperscript{0} atomically dispersed in the crystal, or Pb\textsuperscript{0} precipitated as a separate phase (in a colloidal form) could probably be detected.

9.4.4 Effect of \(\gamma\)-Irradiation on Crystals Grown From Solutions in which PbCl\textsubscript{2} was Added

No conclusive explanation can be offered for the experimental observation that gamma-irradiation does not produce crystals with reduced dislocation densities
when the crystals were grown from solutions containing $10^{-7}$ moles PbCl$_2$/mole KCl; in other words, why dislocation climb is not observed (under irradiation) when the Pb$^{++}$ concentration in the crystal is about $8 \times 10^{-5}$ moles/mole KCl (i.e., about $1.3 \times 10^{18}$ atoms Pb$^{++}$/cm$^3$), while it is observed when the Pb$^{++}$ concentration is $2 \times 10^{-5}$ moles/mole KCl (i.e., about $3.2 \times 10^{17}$ atoms Pb$^{++}$/cm$^3$).

A possible explanation may be that at the higher Pb$^{++}$ concentration, Pb (under the ion or metal form) is collected at the dislocations, making their climb more difficult.

That impurities can impede the climb of dislocations was assumed first by Boas (17). Mott (29) suggested that this is due probably to the adsorption of impurity atoms at the dislocation jogs. It was mentioned earlier that jogs are instrumental in the climb process, being the points where vacancies "condense" or "evaporate" at the dislocation. Thereby such an adsorption of the impurity could prevent or slow down the dislocation climb.

Absorption spectra of the above crystals, as well as etching of crystals grown under irradiation from solutions with higher lead concentration, would be very informative.
CHAPTER 10
RESULTS AND DISCUSSION
EFFECT OF GAMMA-RADIATION ON THE
GROWTH RATE OF KCl CRYSTALS

10.1 Results
The experimental procedure, which was followed for the growth of KCl crystals under $\gamma$-irradiation, is described in Section 6.4. In the present section, the results will be presented along with certain pertinent comments explaining the motivation for obtaining each set of data.

The interpretation and discussion of the data will follow in Section 10.2.

10.1.1 Crystal Growth Rates with $\gamma$-Irradiation Compared with Growth Rates without Irradiation

The results of growth rate measurements under $\gamma$-irradiation are presented in Table 10-1.

A different solution was used for each run; from each "mother" solution crystals were grown under identical conditions, both inside and outside the radiation field.

The number assigned to the crystals for each run indicates the order with which the experiments were performed; for instance, in Run B-10, first a crystal (No. 1) was grown without irradiation, and subsequently another crystal (No. 2) was grown from the same solution, but this time under irradiation.
### TABLE 10-1

Growth Rates of (100) Face of KCl Crystals under Gamma-Irradiation

<table>
<thead>
<tr>
<th>Solution (Run) No.</th>
<th>Crystal No.</th>
<th>Concentration of Added PbCl₂ Moles/Mole KCl</th>
<th>Irradiation Dose Rate Rad/Min</th>
<th>Growth Rate of (100) Faces µ/hr</th>
<th>Supersaturation %</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-10</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>89 ± 10</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2400</td>
<td></td>
<td>89 ± 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-12</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>94 ± 10</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2400</td>
<td></td>
<td>104 ± 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-17</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>37 ± 10</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2400</td>
<td></td>
<td>30 ± 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-18</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>116 ± 12.5</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2400</td>
<td></td>
<td>105 ± 12.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-20</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>44 ± 10</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2400</td>
<td></td>
<td>42 ± 7.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-13</td>
<td>1</td>
<td>1.2 x 10⁻⁷</td>
<td>0</td>
<td>148 ± 12.5</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2400</td>
<td></td>
<td>52 ± 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-15</td>
<td>1</td>
<td>1.2 x 10⁻⁷</td>
<td>0</td>
<td>111 ± 10</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2400</td>
<td></td>
<td>47 ± 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-16</td>
<td>2</td>
<td>1.2 x 10⁻⁷</td>
<td>0</td>
<td>99 ± 10</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2400</td>
<td></td>
<td>50 ± 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-21</td>
<td>1</td>
<td>1 x 10⁻⁷</td>
<td>0</td>
<td>54.5 ± 7.5</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2400</td>
<td></td>
<td>39.5 ± 7.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-23</td>
<td>1</td>
<td>1 x 10⁻⁷</td>
<td>0</td>
<td>18.5 ± 7.5</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0</td>
<td>16.0 ± 9.5</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2400</td>
<td></td>
<td>16.0 ± 2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-24</td>
<td>1,2</td>
<td>1 x 10⁻⁷</td>
<td>0</td>
<td>59 ± 10</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5,6</td>
<td>500</td>
<td></td>
<td>41.5 ± 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3,4</td>
<td>2400</td>
<td></td>
<td>36 ± 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-27</td>
<td>2</td>
<td>1 x 10⁻⁷</td>
<td>0</td>
<td>7.5 ± 9.5</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2400</td>
<td></td>
<td>6.5 ± 4.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-32</td>
<td>3,4</td>
<td>1 x 10⁻⁷</td>
<td>0</td>
<td>60.5 ± 7.5</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,2</td>
<td>2400</td>
<td></td>
<td>48 ± 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-33</td>
<td>1 x 10⁻⁷</td>
<td>0</td>
<td>29.5 ± 2.5</td>
<td>0.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2400</td>
<td></td>
<td></td>
<td>25 ± 2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-34</td>
<td>1 x 10⁻⁷</td>
<td>0</td>
<td>36.0 ± 2.5</td>
<td>0.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2400</td>
<td></td>
<td></td>
<td>29.5 ± 2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-11</td>
<td>1</td>
<td>1.2 x 10⁻⁶</td>
<td>0</td>
<td>25 ± 10</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2400</td>
<td></td>
<td>25 ± 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-26</td>
<td>1</td>
<td>1 x 10⁻⁶</td>
<td>0</td>
<td>47 ± 2.5</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0</td>
<td>54.5 ± 2.5</td>
<td>1.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2400</td>
<td></td>
<td>47 ± 2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-31</td>
<td>2</td>
<td>1 x 10⁻⁶</td>
<td>0</td>
<td>126 ± 12.5</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2400</td>
<td></td>
<td>117 ± 12.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average growth rates for the two crystals.
The growth rate measurements were limited to the (100) faces, since only these faces were present in the seed crystal.

Most of the studies were made using solutions with two concentrations of PbCl$_2$; first, solutions in which no PbCl$_2$ was added (i.e., the magnitude of the lead concentration was in the neighborhood of $10^{-8}$ moles/mole KCl), and second, solutions in which $10^{-7}$ moles PbCl$_2$/mole KCl were added. No differentiation is made between solutions to which $1 \times 10^{-7}$ and $1.2 \times 10^{-7}$ moles PbCl$_2$/mole KCl were added; the difference between the two concentrations - i.e., $2 \times 10^{-8}$ - is of the same magnitude as the variability in lead among the various solutions. (See Section 7.1.3b.)

In addition some experiments were made using solutions containing $10^{-6}$ moles/mole KCl.

Section 7.1.3 indicated that different solutions manifested different growth rates under apparently identical conditions (i.e., no radiation and same supersaturation); compare growth rates for crystals B-10-1, B-12-2, B-17-2, B-18-1, B-20-2 on Table 10-1. This was attributed to fluctuation in the impurity content among the "pure" solutions. Consequently, the growth rate of a crystal under irradiation (at a certain supersaturation) should be compared only with the growth rate without irradiation (at the same supersaturation) obtained from the same
solution and not from a different solution.

To eliminate the effect of fluctuations in the impurity level of the solutions, the growth rate under irradiation can be plotted against the growth rate without irradiation from the same solution. If the line passing through these points coincides with the $45^\circ$ straight line, irradiation does not affect the growth rate. If, however, the line lies above the $45^\circ$ line, irradiation accelerates growth, while if it lies below it, irradiation retards growth. The data are plotted in this manner in Figures 10-1 and 10-2.

10.1.2 Growth Rates under Irradiation as a Function of Growth Time (Effect of Total Radiation Dose)

To study the effect of total radiation dose, growth rate measurements were made on crystals grown from the same solution for varying growth periods.

The results for two different levels of supersaturation are presented in Figure 10-3. Both solutions contained $10^{-7}$ moles PbCl$_2$/mole KCl.

10.2 Discussion of the Results

10.2.1 Effect of Total $\gamma$-Radiation Dose on Growth Rate

From the data presented in Figure 10-3, it
FIGURE 10-1
GROWTH RATE OF (100) FACES UNDER IRRADIATION ($R_i$) VS GROWTH RATE WITHOUT IRRADIATION ($R_o$)

NO PbCl$_2$ ADDED
SUPERSATURATION: 0.12%
EACH POINT REPRESENTS A DIFFERENT "MOTHER" SOLUTION
RADIATION DOSE RATE 2400 RAD/MIN
SHOW ESTIMATED ERRORS

NOTE: RATE VARIES DUE TO "NATURAL" IMPURITIES
ADDITIVE PbCl$_2$  $1 \times 10^{-7}$ MOLES/MOLE KCl

SUPERSATURATION VARIATES.

EACH POINT REPRESENTS A DIFFERENT SOLUTION.

RADIATION DOSE RATE:
2400 RAD/MIN

FIGURE 10-2

GROWTH RATE OF (100) FACES UNDER IRRADIATION ($R_i$) vs GROWTH RATE WITHOUT IRRADIATION ($R_o$)
RADIATION DOSE RATE: 2400 RADS / MIN

Each point represents different crystal, each line a different solution

- Supersaturation 0.44% Run B-33
- " 0.48% Run B-34

PbCl₂ concentration 10⁻⁷ moles/mole KCl

Figure 10-3
Growth of (100) faces under irradiation as a function of time
is deduced that the growth of KCl crystals under a radiation dose rate of 2400 rad/min is linear with time for times ranging from 2 to 8 hours. That is, the growth rate is independent of the total radiation dose over the range of 280,000 to 1,100,000 rads.

This experimental evidence indicates mainly that any permanent chemical change in the solution produced by the γ-radiation dose rate of 2400 rads/min (see, for instance, Equation (5-1)) was not significant enough to affect the growth of the crystals.

10.2.2 Effect of γ-Irradiation on the Crystal Growth Rate from Solutions Containing No Added PbCl₂

Section 7.1.3b suggested that solutions in which no PbCl₂ was added still contained about 10⁻⁸ moles PbCl₂/mole KCl from the reagent KCl.

Inspection of Figure 10-1 indicates that γ-irradiation at a dose rate of 2400 rad/min had no significant effect upon the growth rate of crystals grown from such solutions; all the points lie on the 45° degree line.*

* It has been reported in a previous report of this investigation (AEC-TID 19668) that γ-irradiation appeared to increase the crystal growth rate from solutions in which no PbCl₂ was added. It is believed now, however, that this apparent increase resulted from a change in the impurity content of reagent KCl and not the radiation. For more details see Appendix All.
Assuming that irradiation could affect crystal growth rate only through the "surface" resistance and not the liquid diffusional resistance of the crystallization process, the absence of effect indicates (a) either the mass transfer process through the liquid phase is the controlling rate, or (b) the γ-irradiation did not affect the "surface" rate, i.e., the rate of attachment of the solute atoms at the crystal surface.

However, from experiments discussed in Section 7.1.3(c), the mass transfer process in the liquid phase was concluded not to be the controlling step under the conditions of the above growth experiments (i.e., stirring rate higher than 850 rpm and growth rate lower than 150 μ/hr). Therefore, it appears that Co-60 γ-irradiation at a dose rate of 2400 rad/min does not significantly affect the rate of attachment of the solute atoms at the surface of crystals when the solution contains 10⁻⁸ moles PbCl₂/mole KCl.

This conclusion is not inconsistent with the experimental fact that the dislocation densities of the same crystals were reduced by irradiation for the following reason: In Sections 3.5.4 and 4.1.3 mechanisms were presented, according to which a reduction in the dislocation density may reduce the growth rate. However, this reduction concerns only the number of the screw-type dislocations, since according to the dislocation growth theory
only screw dislocations are important for the crystal growth process. (See Section 3.5.4.) The etching, on the other hand, reveals in general both screw and edge dislocations. A reduction in dislocation density does not necessarily mean that the number of screw dislocations has been reduced. Actually, in the case of the irradiated KCl, the reduction in dislocation density may result only from the reduction of the number of the edge dislocations. It has been theorized above (Section 9.4.3) that this reduction is a result of a dislocation climb process. However, it is well known that only edge dislocations can climb (32). Thus, the number of the screw dislocations formed in a KCl crystal is assumed not to be affected by the γ-irradiation.

In conclusion, γ-irradiation at a dose rate of 2400 rad/hr had no effect on the growth rate of KCl crystals grown from solutions containing 10^{-8} moles PbCl₂/mole KCl.

10.2.3 Effect of γ-Irradiation on the Growth Rate from Solutions in which PbCl₂ was Added

Figure 10-2 (Curve A) indicates that γ-irradiation (2400 rad/min) decreased the growth rate of KCl crystals grown from solutions containing 1 x 10^{-7} moles PbCl₂/mole KCl. This decrease was negligible for growth rates up to 30 μ/hr, but above this value the rate of growth under irradiation became significantly lower than the rate of growth without irradiation from the same
solution. Growth rates without irradiation higher than 160 μ/hr could not be obtained, since above this value the crystals were growing as dendrites.

Irradiation did not have a significant effect if the lead concentration in the solution was $1 \times 10^{-6}$ moles/mole KCl. Curve B does not differ significantly from the $45^\circ$ line.

Only two runs with solutions of this concentration were successfully completed. Other runs performed at conditions adjusted to give growth rates higher than 70 μ/hr were not successful; very irregular crystals were obtained and the solution nucleated before the end of the run. It is suspected that the stirring rates used (770-900 rpm) corresponded to the critical stirring rate at which the mass transfer process of the lead ions in the liquid becomes important. It can be recalled from the discussion in Section 7.2.3d that when the diffusion of lead becomes the controlling step, the crystals grow in an irregular shape (formation of crystallites on their surface) and at the same time secondary nucleation results. Higher stirring rates were necessary to overcome this problem. However, this was not possible with the experimental set-up used for the runs under irradiation.

A mechanism which would explain the effect of radiation in decreasing the growth rate in solutions containing $1 \times 10^{-7}$ moles PbCl$_2$/mole KCl should also explain
why the same radiation dose rate did not affect the growth rate at the $10^{-8}$ and $10^{-6}$ moles Pb/mole KCl level. A possible mechanism will be suggested and discussed in the next section. First, however, the following two possibilities will be ruled out:

a) that the growth retardation is the result of chemical changes in the solution by the $\gamma$-rays. Indeed, chlorine has been detected(23,101) in irradiated solutions of KCl, as one of the radiolysis products. Chlorine formation results in the reduction of the concentration of the solute and consequently of the supersaturation. However, if this reduction in supersaturation was appreciable, the growth rate in solutions with no added PbCl$_2$ or solutions containing $10^{-6}$ moles PbCl$_2$/mole KCl should also be affected by the irradiation.

b) that an increase in the temperature in the crystallizer by the absorbed $\gamma$-radiation is responsible for the observed reduction in growth rate. The heat absorbed by the solution in the crystallizer is dissipated through the constant temperature bath in which the crystallizer is immersed. However, it is possible that a temperature gradient develops between
the crystallizer and the bath.* A higher temperature in the crystallizer means a lower supersaturation and thereby a decrease in growth rate. This possibility, however, is also excluded since such a temperature rise (or decrease in supersaturation) would have affected to the same extent the growth rate of crystals from solutions containing no added lead (compare curves B and C in Figure 7-9).

10.2.4 Suggested Mechanism - Effect of γ-Irradiation on the Diffusion of Lead through the Crystal Bulk

The growth rate (in the absence of irradiation) in solutions containing $10^{-7}$ moles Pb/mole KCl was decreased in comparison to the growth rate in solutions in which no PbCl$_2$ was added (see Figure 7-9). This has been attributed to the adsorption of lead ions on the surface and the subsequent retardation of the growth steps. Under γ-irradiation the difference in crystal growth rate between solutions containing no added lead and $10^{-7}$ moles PbCl$_2$/mole KCl became larger. It is suggested

* A platinum resistance thermometer was used to record the temperature in the crystallizer (see Section 6.4.2). An increase in the solution temperature was not observed under irradiation. However, the sensitivity of the instrument was such that only temperature changes higher than $0.03^\circ C$ could have been detected.
that under irradiation the concentration of the lead ions on the crystal surface increased and as a result the growth rate decreased further.

The hypothesis is made that such an increase results from the following mechanism: \( \gamma \)-irradiation increases the diffusion rate of the lead in the bulk of the crystal towards the surface. The lead diffuses towards the interface since, as it was assumed in Section 8.3.2, it is included in the crystal in concentrations higher than the equilibrium.

The indications on which the above hypothesis is based will be discussed next.

It was pointed out in Section 3.4.1c that diffusion in solids takes place mainly via defects, namely vacancies and interstitials. It has been suggested (37) also that diffusion may be enhanced along individual dislocations. Direct evidences for such a "dislocation-pipe" diffusion has not been presented yet; however, indirect indication of the effect exists in the case of metals (37).

High energy irradiation produces such defects; therefore, it is expected to affect the diffusion process.

The influence of excess vacancies formed by irradiation on the diffusion through a solid has been investigated by studying the rate of ordering of alloys possessing an ordered state. Thus Dugdale (62) has studied the effect
of $\gamma$-irradiation on the ordering of partially disordered Cu$_3$Au. He found this to be increased appreciably under $\gamma$-irradiation.

The actual atomic mechanism of the diffusion process of lead in the KCl crystals is not known. It could be either through vacancies and interstitials or along dislocation lines. Even in the latter case, however, vacancies or interstitials may play a role. In order to diffuse along a dislocation, lead has to migrate from the various points of the lattice to the dislocation line; and this process may take place through point defects.

Gamma-irradiation of KCl crystals increases considerably the number of point defects (vacancies and interstitials) in the crystals. (See Appendix A9.1 and Section 5.3.2.) Enhancement of the rate of diffusion of lead is, thus, probable. The question is now how much such an increase in the point defect concentration would enhance the diffusion of lead towards the crystal surface. Since the mechanism of the lead diffusion process is not known, the question cannot be answered quantitatively. However, certain indicative calculations will be presented.

The diffusion coefficient of lead ions in KCl, $D_{\text{Pb}^{++}}$, was calculated to be $3.8 \times 10^{-19}$ cm$^2$/sec (see Appendix A7). Let it be assumed, for the sake of the argument, that diffusion of lead in KCl crystals occurs by means of vacancies (other than the charge-compensating vacancies,
which are associated with the lead ions). Then, according to Equation (3-18),

\[ D_{\text{Pb}^{++}} = D_0^* C_v e^{-\frac{E_m}{RT}} \]  

where \( C_v \) = atomic fraction of vacancies.

Under \( \gamma \)-irradiation, however, there is, in addition to the equilibrium concentration \( C_v \), a steady-state concentration of vacancies \( C_v^{\text{irr}} \) created by the irradiation and depending on the flux \( \phi \). This leads to the following diffusion coefficient (57):

\[ D_{\text{Pb}^{++}}^{\text{irr}} = D_0^* \left[ C_v + C_v^{\text{irr}}(\phi) \right] e^{-\frac{E_m}{RT}} \]  

Dividing (10-1) by (3-18), the following equation is obtained:

\[ D_{\text{Pb}^{++}}^{\text{irr}} = \frac{D_{\text{Pb}^{++}}}{C_v^{\text{irr}}(\phi)} \]  

The equilibrium vacancy concentration \( C_v \) at 35°C in KCl is 1.4 \( \times 10^3 \)/cm\(^3\) (see Section 3.4.1).

To calculate \( C_v^{\text{irr}}(\phi) \), it is assumed that for a growing crystal, only the diffusion through a crystal growth layer, during the time the layer is the top layer, is important.

In KCl the growth layer (from solutions containing
10⁻⁷ moles PbCl₂/mole KCl) was assumed to be 25 Å. (See Section 8.3.2.)

For a growth rate of 100 microns/hr, the time between two successive layer depositions is 1.5 x 10⁻³ min. The rate of displacement production at the radiation dose rate of the present investigation is 1 x 10¹⁵ displ/cm³/min. (See Appendix A9.1.) Assuming no annealing at 35°C, the concentration of vacancies produced by the irradiation in the top layer is 1 x 10¹⁵ x 1.5 x 10⁻³ = 1.5 x 10¹²/cm³.

Substituting in Equation (10-2), it is found that

\[ D_{\text{Pb}^{++}}^{\text{irr}} = 3.8 \times 10^{-19} \times \frac{1.5 \times 10^{12}}{1.4 \times 10^3} = 4 \times 10^{-10} \text{cm}^2/\text{sec} \]

which is about nine orders of magnitude higher than \( D_{\text{Pb}^{++}} \) at 35°C. Actually it is equal to the \( D_{\text{Pb}^{++}} \) without irradiation at about 400°C.

To compare the two diffusion coefficients, the time required for the diffusion of lead through the top layer (25 Å), \( t = \frac{(\text{distance})^2}{D_{\text{Pb}^{++}}} \), is estimated.

Without irradiation the time is of the order of 10³ min., while under irradiation of the order of 10⁻⁶ min. The first is about six orders of magnitude higher than the time a growth layer remains as the top layer (1.5 x 10⁻³ min for the particular growth rate), while the second is about three orders smaller. In other words,
the above value indicates that under $\gamma$-irradiation the lead has sufficient time to diffuse to the crystal surface.

The value of $10^{-6}$ min appears to be low, probably due to the simplifying assumptions made. However, this value could be considered as an indication that enhanced diffusion of lead through the solid under irradiation is a plausible mechanism to account for the assumed increased lead concentration at the crystal surface.

The suggested mechanism is consistent with the following:

a) the observation that $\gamma$-irradiation did not affect the growth rate at the $10^{-8}$ moles Pb/mole KCl level.

It can be recalled that in this case the dislocation density decreased, and the vacancies created by the $\gamma$-rays were "consumed" in the assumed dislocation climb process. (See Section 9.4.3.) Thus, no enhancement in the diffusion rate of lead in the crystal is expected, and thereby no increase in the impurity concentration at the surface. A dislocation climb did not take place in crystals grown from solutions containing $10^{-7}$ moles PbCl$_2$/mole KCl.

b) the form of the curve A in Figure 10-2

This curve shows that the difference between the growth rate with irradiation and that without irradiation increases faster (i.e., the slope of the curve A decreases appreciably) when a growth rate (without irradiation) of about 60 to 70 $\mu$/hr is reached.
Let it be assumed that irradiation increases the lead concentration on the crystal surface. In the diagram crystal growth vs. supersaturation (see Figure 7-9), an increase in the lead concentration on the crystal surface corresponds to a shift of the curve to a new position to the right. Even in the case of a small shift, the difference between the growth rates in the old and new position, for each supersaturation, increases sharply above the point where the curve becomes almost parallel to the ordinate. For solutions containing $10^{-7}$ moles Pb/mole KCl (curve B in Figure 7-9), this point is around 60 to 70 μ/hr; this is in agreement with the data (curve A, Figure 10-2).

c) the observation that γ-irradiation had not a significant effect on the growth rate of crystals in solutions containing $10^{-6}$ moles Pb/mole KCl (curve B, Figure 10-2).

The suggested mechanism predicts that for such solutions, the slope in the curve "growth rate with irradiation" vs. "growth rate without irradiation" would start decreasing appreciably only at growth rates of about 130 μ/hr. This means that, according to the above mechanism, the effect of radiation is not necessarily significant for crystals growing slower than 130 μ/hr. However, the effect of radiation would have been significant with crystals grown at a rate higher than 130 μ/hr.
Attempts to grow crystals at this growth rate region failed for reasons explained above (Section 10.2.3).
The highest growth rate in the experiments with solutions of $10^{-6}$ moles Pb/mole KCl was 126 $\mu$/hr. (See curve B, Figure 10-2.)

In conclusion, the data are not quite sufficient to prove the assumed mechanism, i.e., that the lead concentration on the crystal surface was increased as a result of an enhancement of the rate of lead diffusion in the crystal by the irradiation. However, this mechanism offers consistent possible explanations about the effect of irradiation for all three levels of impurity.

10.3 Future Work with Irradiation

The idea which initiated this investigation was to create dislocations in a growing crystal, by high energy radiation, and to study their effect on the growth rate of the crystal. In other words, the crystal growth experiments under irradiation would be a direct test of the dislocation growth theory.

Neutrons and $\gamma$-rays have a satisfactory penetrating power for irradiating a crystal inside a solution. Neutrons can produce dislocations in a crystal through formation of spikes. (See Section 5.2.2.) However, the cost of carrying out experiments with neutrons was prohibitive. For this reason $\gamma$-rays from a Co$^{60}$ source were
chosen. Gamma-rays have not been found to produce dislocations in dry crystals. It was hypothesized, however, that in a growing ionic crystal, the large number of vacancies produced by the $\gamma$-rays would probably coalesce to form a monolayer vacancy precipitate; this precipitate would subsequently collapse and form a dislocation loop. (See Section 3.4.2.)

This initial idea failed to be tested by the growth experiments of this investigation for the following reasons: first, the dislocation density in KCl crystals grown from the solution was already very high ($10^7/cm^2$); and second, in solutions containing no added PbCl$_2$, the vacancies formed were absorbed in the existing dislocations and new ones were not produced.

For these reasons, a future investigation should involve crystallization processes which, without irradiation, would produce crystals with low dislocation densities. Such processes are crystal growth from vapor and whisker crystal growth. The latter process for KCl is described in detail in Appendix A17.

The two effects of the $\gamma$-radiation on KCl crystals discussed in Chapters 9 and 10, i.e., the observed production of crystals with lower dislocation density under irradiation than without, and the assumed enhancement of the impurity diffusion rate in the crystal under irradiation, appear also to be very promising for further investigation.
A study of the reduction in dislocation density, presumably by a climb process, will be of interest to solid state physicists. (All their previous studies were made with dry crystals.) It will probably elucidate further the nature and the interaction of the various atomic defects formed during irradiation of ionic crystals containing multivalent impurities. Certain experiments were suggested in Section 9.4.3. This reduction is not high enough to be of practical significance in the production of low dislocation density crystals. The possibility, however, should be examined that very low growth rates and growth of crystals nucleated in the solution (and not seed crystals as in this investigation) would lead to very low dislocation densities.

The assumed enhancement of the diffusion rate of the impurity under irradiation should be further tested. Such a phenomenon may have an important application in the "doping" of certain crystals. High temperature is used now to enhance the diffusion of the impurity. Irradiation presents the advantage that diffusion can be enhanced only in the region of the crystal which is exposed to irradiation.
CHAPTER 11

CONCLUSIONS AND RECOMMENDATIONS

11.1 Concluding Remarks

The observed properties of lead a) to retard growth on the (100) face of the KCl and b) to be incorporated into the growing crystal, as well as the effect of the radiation in decreasing the growth rate in solutions containing $10^{-7}$ moles Pb/mole KCl, were attributed to the following:

a) Lead ions are strongly adsorbed at the planar regions between growth steps on the (100) face of the KCl crystal. (Cabrera mechanism—see Section 4.1.3.)

b) The concentration of lead at the surface is larger than the concentration of lead in the solution as well as the equilibrium concentration of the lead in the bulk of the crystal. (See Section 8.3.2.)

c) The diffusion coefficient of lead in the crystal of KCl at 35$^\circ$ (the crystallization temperature) is extremely small.

Any other impurity satisfying the above three conditions is assumed to give rise to the same phenomena as lead.

The adsorption of lead on the crystal surface is probably associated with the formation of a complex. Metal ions which do not retard growth presumably do not
form such a strong complex on the surface. For other ions the favorable sites for complex formation are the kinks at the growth steps. (Sears mechanism - see Section 4.1.3.) If this complex is mobile, it will be carried along with the advancing steps, and no incorporation will take place, although growth retardation is possible.

This investigation did not try to answer why some metal ions form a strong complex on the surface (i.e., they retard growth and are incorporated), while others form a complex at kinks (i.e., they retard growth without being necessarily incorporated), or others do not form any with a given crystal surface (i.e., they do not retard growth). In other words, no attempt was made to establish criteria for predicting the behavior of a particular ionic impurity in a given crystal. For this, additional growth rate and incorporation data for other ions and crystallizing species are needed. These data combined with the coordination properties of each ion will hopefully elucidate the formation of the impurity complexes on the crystal surface, and their effect on the growth rate and the purity of a crystal.

11.2 Conclusion

The principal conclusions reached during this study can be summarized as follows.
11.2.1 Growth of KCl Crystals without Irradiation

i) Lead chloride decreased the growth rate of the (100) faces of KCl even in solutions containing as low as $10^{-8}$ moles PbCl$_2$/mole KCl. The decrease became more important as the PbCl$_2$ concentration increased and the supersaturation level decreased.

ii) Reagent grade KCl, used for the preparation of the supersaturated solutions, was found to contain lead at the level of $10^{-8}$ moles/mole KCl. Thus, growth rates from a truly pure solution have not been obtained.

iii) Growth rates (with or without added lead) of KCl crystals increased rapidly with supersaturation level. The change to rapid dendritic growth occurred within a very small supersaturation range, for instance from 0.17 to 0.20% supersaturation for a solution containing no added PbCl$_2$. The drastic increase is consistent with Cabrera-Frank's model of time-dependent adsorption of impurities on a crystal surface.

iv) Crystal growth rates were not mass transfer controlled except at high supersaturations when dendritic growth occurred, or when low stirring rates were employed.

At low stirring rates either the mass transfer of the principal solute (KCl) became controlling (in solutions without added lead) or the mass transfer of the impurity lead (in solutions with added lead). In the former case, the growth rate decreased, and in the latter
increased as the stirring rate decreased.

v) Secondary nucleation always accompanied the formation of dendrites. The idea that secondary nuclei originate from broken dendritic branches is thus supported.

11.2.2 Growth of KCl Crystals in a γ-Radiation Field

1) Effect of γ-Irradiation on Dislocation Density

Potassium chloride crystals grown under Co\textsuperscript{60} γ-irradiation (dose rate 2400 rad/min) from solutions containing no added PbCl\textsubscript{2} showed a slightly reduced dislocation density relative to crystals grown from the same mother solution but without irradiation.

It is suggested that a dislocation climb process is responsible for the observed reduction.

Irradiation had no effect on the dislocation density of crystals grown from solutions containing 10\textsuperscript{-7} moles PbCl\textsubscript{2}/mole KCl.

ii) Effect of γ-Irradiation on the Growth Rate

Irradiation of 2400 rad/min dose rate had no effect on the growth rate of the (100) faces of KCl crystals grown from solutions containing no added PbCl\textsubscript{2} and solutions containing 10\textsuperscript{-6} moles PbCl\textsubscript{2}/mole KCl.

However it decreased the growth rate of the (100) faces relative to the rate at the same impurity level, when the lead concentration in the solution was 10\textsuperscript{-7} moles/mole KCl.
11.2.3 Incorporation of Impurities during KCl Crystal Growth (without Irradiation)

i) Potassium chloride crystals grown from solutions containing lead ions in concentrations less than $10^{-5}$ moles Pb/mole KCl will contain a higher concentration of lead than in the crystallizing solution.

ii) Lead distribution coefficients, crystal-to-solution, ranged from 2700 to 28. The coefficients decreased as the lead concentration was increased.

iii) For a given constant lead concentration in the solution (i.e., $10^{-7}$ moles/mole KCl), the lead concentration in the KCl crystals decreased as the growth rate increased.

iv) The incorporation of Fe$^{+++}$, Ti$^{+++}$, Bi$^{+++}$, Hg$^{++}$ by the growing KCl crystals was also tested. For certain solution concentrations, iron and titanium presented effective distribution coefficients larger than unity; bismuth and mercury did not under any of the concentrations used.

v) The results indicate that in order to produce ultrapure crystals of KCl (free from Pb$^{++}$ and Fe$^{+++}$), the conventional techniques of recrystallization should be modified to include rejection of the first crystals grown.
11.3 Recommendations

11.3.1 Study of Crystal Growth Rates in Presence of Ionic Impurities

It is recommended:

i) that future growth experiments be conducted with a flow recycling apparatus. (See Appendix A15.1.)

ii) that the growth rate of the (100) faces of KCl at extremely low lead concentrations (\(<10^{-8}\) moles/mole KCl) be determined.

iii) to study quantitatively the absolute growth rates of the various faces of KCl as well as other ionic salts in the presence of various ionic impurities. These data combined with impurity incorporation data would answer the question why certain metal ions are adsorbed on a crystal face and others are not. Also, which of the impurities adsorb at the growth steps and which on the flat crystal surface. The use of radioactive tracers and autoradiographs will be very helpful.

11.3.2 Crystal Growth Studies under Irradiation

It is recommended:

i) to study the effect of high-energy radiation on the growth rate of crystals growing from vapor and on the whisker crystal growth.

ii) to evaluate the possibility that the assumed enhancement of diffusion rates in a crystal under
irradiation can find an application in the doping of crystals.

iii) to elucidate the mechanism by which crystals with lower dislocation density are produced under irradiation and also determine the conditions under which the dislocation density can be reduced appreciably (several orders of magnitude).

1. by using various multivalent ionic impurities
2. by obtaining the absorption spectra of the irradiated crystals
3. by conducting the experiments in the dark
4. by irradiating crystals nucleated in the solution (no seed crystals)
5. by studying the dependence of the dislocation density under irradiation upon the crystal growth rate.

11.3.3 Study of Impurity Uptake by Crystals
It is recommended in a future study:
1) to verify that the above suggested recrystallization process produces KCl crystal free of Pb and Fe.
2) to calculate theoretically the solubility of lead and ferric chlorides in alkali halides.
3) to extend the impurity uptake investigation to
other reagents, especially those for which a high impurity content is reported.

iv) to investigate the incorporation of various ionic impurities along the various faces of given ionic salts. These data combined with growth rate data, and x-ray and optical absorption spectra, would probably establish criteria for predicting the uptake or not of a given impurity by a growing crystal.
APPENDIX A1
SOLUBILITY DATA FOR KCl

The solubility data for potassium chloride were taken from the "Salinities of Inorganic and Metal Organic Compounds" by A. Seidell, Ed. 2, Vol. 1, p. 747, VanNostrand Co., Inc., N.Y. 1940.

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<th>Solubility (g/Kg of Water)</th>
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APPENDICES

To calculate the supersaturation, however, the solubility was expressed in g/Kg of water. The specific gravity used in the conversion was found by extrapolation of the values in the "Handbook of Chemistry and Physics", C.D. Hodgman, Editor, 25th Edition.

The values used for the supersaturation calculations are given in the following table.
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To calculate the supersaturation, however, the solubility was expressed in gms/liter. The specific gravity used in the conversion was found by extrapolation of the values in the "Handbook of Chemistry and Physics", C.D. Hodgman, Editor, 25th Edition.

The values used for the supersaturation calculations are given in the following table.
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<th>gm/liter Soln.</th>
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### CHEMICAL ANALYSIS OF POTASSIUM CHLORIDE

The chemical analysis given by the manufacturer (J.T. Baker Chemical Co.) for the reagent KCl is the following:

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<td>pH of 5% Solution at 25°C</td>
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<td>Heavy Metals (as Pb)</td>
<td>0.0002%</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>0.00005%</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>0.003%</td>
</tr>
</tbody>
</table>
A3.1 Description of crystal measurement procedure

It can be seen in Figure 6-2 that a crystal is free to grow only in the direction of length (L) and height (H) but not in the direction of width (W). Therefore only the measurements of the length and the height of a crystal before and after the growth were used to determine the growth.

The procedure was to measure the length and the height on the one face, turn over the crystal and repeat the measurements on the opposite side. Then the height was measured on one of the side faces. At the end of the growth experiments, the measurements were repeated at the same points of the crystal. The increase in the dimensions of the crystal was obtained by subtraction. The two values for the length and the three values for the height were averaged and finally one value for the length and another for the height were obtained (L and H in Appendix A14).

To obtain the growth rate of the (100) face of the crystal, the average of the above two values was divided by 2 and by the time of growth.

A3.2 Depletion of the solution with respect to KCl and PbCl₂

Depletion of KCl

The crystal B-42(1) will be considered here:
Volume of crystal before growth = \((88.5 \times 37 \times 81)\) cubic units
Volume of crystal after growth = \((95.5 \times 44 \times 88)\) cubic units
1 unit = 24.7 microns
1 cubic unit = \(1.5 \times 10^{-8}\ \text{cm}^3\)
Density of KCl = 1.99 gm/cm\(^3\)

Therefore
weight of crystal before growth = \(8 \times 10^{-3}\) gm
after growth = \(11 \times 10^{-3}\) gm
Depletion of solution = \(3 \times 10^{-3}\) gm

Depletion due to 10 crystals \(30 \times 10^{-3}\) gm; change in supersaturation due to depletion 0.009. This corresponds to change in the temperature of the bath of 0.015\(^\circ\)C. Hence the change in supersaturation due to depletion is within the order of change due to the temperature variation in the bath.

Depletion of PbCl\(_2\)
Lead content of the crystal (see Table 8-1) = \(78 \times 10^{-6}\) moles PbCl\(_2\)/mole KCl
Lead content of the solution = \(10^{-7}\) moles/mole KCl
Crystal grown (for 10 crystals) = \(30 \times 10^{-3}\) gms or \(4 \times 10^{-5}\) moles KCl
KCl in the solution \(\approx 332\) gm or 4.5 moles.

Total lead in solution \(4.5 \times 10^{-7}\) moles
lead in crystal \(4 \times 78 \times 10^{-11} = 3.1 \times 10^{-9}\)
Depletion in lead by the 10 crystals = 0.7\%
A3.3 Addition of PbCl₂ - Preparation of additive solution

To bring the concentration of lead in the supersaturated solution at the desired level, one drop of a stock PbCl₂ solution was added to the crystallizer.

For a $10^{-7}$ moles PbCl₂/mole KCl concentration in the solution, the following stock solution was prepared.

Volume of solution in crystallizer = 1055 cc
Concentration of KCl in a solution saturated at 35.7°C = 333.4 gm/liter
Total KCl in crystallizer = 351.7 gm or 4.7 moles
Moles of additive required = $4.7 \times 10^{-7}$
Since this amount should be contained in one drop (20 drops = 0.8 cc) the concentration of the solution should be

$$\frac{4.7 \times 10^{-7} \times 278.1 \times 20 \times 1000}{0.8} = 3.27 \text{ gm/lit.}$$

A3.4 Performance of the crystallization apparatus inside the radiation field

In the growth experiments inside the radiation field the solution in the crystallizer absorbs heat directly from the radiation. This heat is dissipated by the constant temperature bath. However, it is possible that a temperature gradient would develop between the crystallizer and the bath.

The difference in temperature between bath and crystallizer will be calculated:
Volume of solution = 1055 cc
Weight of solution = 1250 gm
Weight of glass = 300 gm
Total surface = 570 cm²
Heat transfer coefficient U = 0.9 cal/cm²°C/min (measured)
Radiation dose rate = 2400 rad/min

Heat absorbed by the crystallizer \((1550 \times 2400 \times 100 \times 2.39 \times 10^{-8}) = 8.9 \text{ cal/min}\)

Therefore \(\Delta t = \frac{8.9}{0.9 \times 570} = 1.7 \times 10^{-2} \text{°C.}\)

However, the temperature of the bath will be lower inside the radiation field than outside for the same setting of the mercurial regulator. The reason is that the mercury reservoir will absorb heat not only from the bath but also directly from the γ-rays. The difference in temperature between bath and reservoir can be calculated.

Volume of reservoir = 3.14 cm³
Area of reservoir = 12.6
Heat absorbed = \((3.14 \times 13.6 \times 2400 \times 100 \times 2.39 \times 10^{-8}) = 0.24 \text{ cal/min}\)

\(\Delta t = \frac{0.24}{0.9 \times 12.6} = 2.1 \times 10^{-2} \text{°C.}\)

Hence the two effectively balance each other and the solution in the crystallizer will have a temperature differing less than 0.005°C from the temperature it had outside the radiation field for the same setting of the regulator.
A3.5 Determination of the radiation dose rate

The source of the Nutrition, Food Science and Technology Department of MIT was installed in October 1961. At that time, the dose rates were determined at various points inside each container. Fricke dosimetry (oxidation of ferrous ammonium sulfate) was used. From the values, tables were constructed (on a 5.2 years half-life for Co-60) mapping the radiation dose rates at the various points for the later dates. These values are checked periodically by the personnel of the source. The values found are always within 10% of those calculated from the table.

The same agreement was found during this investigation by Arthur Hill of the Chemical Engineering Department, who measured dose rates at certain points on March 19, 1963. Hence the values in the tables can be used with confidence.

An average value was used for the calculation in this report: 2400 ± 200 rad/min

The variation is due to the following:

a) In the area where the crystals were grown the dose rate varied locally; for instance from a minimum 2310 in a point to a maximum of 2440 rad/min in another point

b) The crystal growth experiments were conducted in a time period ranging from December 1963 to May 1964; a dose rate of 2440 in December 1963 would correspond to 2310 rad/min in May 1964.
c) The dose rate would increase by about 3.5% when the center box (see Figure 6-3 - a side box was used during this investigation) was at the bottom of the tank.

The center box was used by other investigators and for this reason no control could be exercised on its position.

APPENDIX A4

ETCHING OF KC1 CRYSTALS

A4.1 Theory of etching

The etching process is based on the property of an etching solution to attack a crystal surface at discrete points: i.e. where dislocations meet the surface. This is explained by the extra energy localized around the dislocation. Less energy is required to remove an atom from the surface of the solid near the dislocation than from any other point of the surface (98).

The inverted pyramidal form of the etch pits on the KC1 crystal surface is explained as follows: When a crystal surface is exposed to a solvent, dissolution probably begins by the nucleation of "unit pits" of one molecule depth (Figure A4-0,a). These unit pits grow as steps retreat through the crystal.

On a perfect crystal face the nucleation of unit pits is random. On a real crystal dislocations provide
preferential sites for nucleation of unit pits. However, while the step retreats, the nucleation is repeated at the dislocation line. This repeated nucleation leads to the formation of an etch pit, at the point of the surface where a dislocation line emerges (Figure 9-1,b).

Figure A4-0

It should be noted that etch pits are formed in both the points where edge dislocations and screw dislocations emerge. The only difference will be that in the latter case the inner stepped surface of the pit is of spiral form. In most of the cases, however, (including KCl) the height of the steps is such that it cannot be observed by an optical microscope.

Thus the dislocation density measured on the KCl crystals by an etching technique includes both screw and
edge dislocations.

A4.2 The development of an etching technique and of a polishing agent for KCl crystals

A4.2.1 Introduction

The purpose of this present part of the project has been to develop a technique which would yield an accurate determination of the dislocation density in potassium chloride crystals. Ultimately, the technique will be used to determine such dislocation densities in crystals grown both under radiation and without a radiation in an attempt to correlate differences in crystal growth rates. Many different etching solutions were screened and it was found that methanol saturated with ammonium chloride was the most promising one. This etchant solution has been reported previously in the literature by Anokhina et. al. (5) and also by Kolontsova and Kulyavik (106), but there has been no attempt to optimize the conditions under which this etchant might be used; this report presents a detailed study of such optimum conditions.

Often crystals grown from solution have superficially rough surfaces. Before such crystals may be etched and dislocation densities determined, one must first prepare the crystals so that it has a smooth surface. To accomplish this a polishing agent is required. Several polishing agents were studied and tentative conclusions indicate that either ethanol-water or a complex mixture suggested
in the Russian crystallographic literature will serve the purpose desired for the present work.

A4.2.2 Detailed description of etching technique

a) Preparation of the Etch Solution

A glass stoppered Pyrex bottle is thoroughly cleaned and dried in an oven overnight. The bottle is washed with cleaning solution and rinsed thoroughly with both distilled water and triply-distilled water. The bottle containing the ammonium chloride, unstoppered, is placed in a desiccator for two or three days. Reagent grade methanol is added to the bottle and the solution is heated and agitated and then allowed to stand overnight while stoppered.

b) Cleavage of the Crystal

The small crystals used for etching were obtained by cleaving a large crystal* in the following way. The crystal is held gently in stainless steel tweezers and a stainless steel razor blade is touched to the edge of the crystal. By moving the blade gently from one side to the other, most crystals cleave cleanly. The blade should in no case be forced downward into the crystal as this will leave considerable irregularities on cleaved surface. With some care surfaces of cleanly cleaved crystals should be similar to that shown in Figure A4-1. The "steps" occur probably because the razor blade was not held exactly parallel to the 100 face at the time of cleavage. It has

*The crystal was grown from melt at the Insulation Laboratory MIT.
also been observed during this study at some dislocations are actually induced by the stress of the razor blade while cleaving the crystal. There appears to be an area of high dislocation density usually found adjacent to the plane where the blade was introduced. This effect should probably be verified quantitatively, and if the observation is valid, larger crystals should be used in the etch studies to reduce the relative area affected by the cleavage process.

c) Etching of Cleaved Crystal

About ten to fifteen ml. of etchant are poured into a small 20 ml. beaker. The beaker should previously have been cleaned in the same manner as was the etchant bottle. The temperature of the etchant is adjusted to be between 26 and 30 degrees centigrade. The upper limit does not appear to be critical but below 26 degrees centigrade, normal dissolution prevails over the desired preferential solution at dislocations. The temperature is most easily controlled by placing the beaker in a water bath. With stainless tweezers the crystal is held in the etch solution for thirty seconds. Caution must be taken to observe the orientation of the cleavage plane during this process. Stirring of the solution does not appear to be necessary. The crystal is rinsed by dipping it into 30-40 ml. of dry butyl alcohol for ten to fifteen seconds. The rinse solution is agitated during this dip. Drying is accomplished with filter paper. If possible, however, care should be
FIGURE A4-1
SURFACE OF CLEAVED CRYSTAL
750X

FIGURE A4-2
TYPICAL ETCHED SURFACE
288X

FIGURE A4-3
CRYSTAL ETCHED WITH 1% FeCl₃ ADDED TO ETCH SOLUTION
750X
taken to avoid touching the cleavage face with the filter paper since this may easily scratch the surface. Once most of the rinse solution is removed, the cleavage face will dry quickly by evaporation. Finally, the cleaved, dry crystal is carefully placed on a microscope slide.

At all times it is extremely important to have the beakers, tweezers, razor blades, and all other materials which come in contact with the crystal surface extremely clean. Trace amounts of impurities will change the etchant performance noticeably. The etchant solution and the rinse solution may be re-used four to six times before it is necessary to discard for fresh solutions. A typical etched surface is shown in Fig. A4-2. The pits are all well formed, and are pyramidal.

Small amounts of impurities may often drastically change cleanliness of etching. For example, the effect of small amounts of FeCl₃ (1%) added to the etch solution is shown in Fig. A4-3. It is obvious that the efficiency of the etch solution was greatly decreased.

d) Etch Pit Density as a Function of Time

From previous work in our Laboratory, it was believed that the number density of etch pits detectable varied quite strongly as a function of etching time and in many cases it was difficult to determine a good mean dislocation density. To verify this tentative conclusion, two crystals were etched at 10 second intervals from 10 to 60 seconds;
pictures were taken under the microscope after each etching. In no case was any real increase in the number of pits noticed. It is possible that in the previous work, where an increased number of pits was observed, crystals were used, in which the distribution in the rate of growth of pits was extremely wide. It is, of course, also possible that the glue used to hold the crystals on the slide halted further nucleation of the pits or that successive butyl alcohol rinses somehow inactivated the surface. One crystal surface is shown in Fig. A4-4 after etch times of 10, 30 and 50 seconds period.* From these photographs and many others taken in this work, it is concluded that etch pit density is not a strong function of etch time at least for times greater than 10 seconds. To allow for sufficient penetration of the etch solution, but not so much that the etch pits would tend to run together, a standard time of 30 seconds was chosen as the optimum time for immersing the crystal in the etch solution.

e) Etchant Reproducibility

To check for etchant reproducibility, several crystals were cleaved and both sides etched and analyzed for mirror image correspondence between etch pits. In Figure A4-5(A,B) are shown acceptable mirror image correspondence.

*The flat-bottomed etch pits are attributed to dislocation loops.
FIGURE A4-4

SURFACE OF CLEAVED CRYSTAL ETCHED
a) at 10 sec, b) at 30 sec,
c) at 50 sec
FIGURE A4-5

COMPARISON OF MATCHED CLEAVAGE FACES (MIRROR IMAGES)

288X
It is obvious, however, from Fig. A4-5 that etch pits corresponding to the same dislocations do not grow at the same rate on the two cleavage faces. The reason for this is not apparent. Perhaps the stress of cleavage affects the energy of dislocations by changing the angle at which the dislocation line meets the cleavage surface. If all dislocations are of the same energy, and the etching takes place by the segregation of ammonium chloride at dislocation sites, the growth of the particular pit would be a function of the probability of ammonium chloride segregating at that site. Due to this difference in growth rate, it becomes increasingly difficult to identify one-to-one etch pit mirror image correspondence as the density of pits increases. However, the same over-all mirror image patterns remain as shown in Figure A4-6 for crystals with a high dislocation density. In addition, the overall dislocation density remains identical on the two faces. One can, therefore conclude that the methanol-ammonium chloride etchant does attack the crystal surface selectively at the points where dislocation lines emerge and that our technique has been perfected so that reproducible etch pit patterns are obtained. These results are in agreement with those found by Predvoditelev and Stepanova, quoted in (106).

A4.2.3 Polishing

It is usually found that the surfaces of crystals grown from solution are very rough and hence unsuitable
FIGURE A4-6

COMPARISON OF MATCHED CLEAVAGE FACES (MIRROR IMAGES). 288X
for direct etching to determine the dislocation density. The cleavage technique cannot be used to produce an etchable surface since the section of the crystal which was actually formed by growth in solution is only on the order of a tenth of mm wide. Therefore, it was found desirable to find a solvent which would attack the crystal surface non-preferentially, remove only a few microns of material, and leave a smooth surface suitable for etching. A number of solutions were investigated and two polishing techniques were finally developed which yielded reasonably satisfactory results. In Table A4.1 the solutions which were investigated and found to give inadequate polishing are presented.

**TABLE A4.1**

**Solutions Giving Inadequate Polishing on KCl Crystals**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1/1</td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
</tr>
<tr>
<td>Potassium Chloride/water</td>
<td>1/20</td>
</tr>
<tr>
<td>Potassium Chloride/water</td>
<td>20/1</td>
</tr>
<tr>
<td>Water with 1.5 wt. % ammonia</td>
<td></td>
</tr>
<tr>
<td>Water with 1.5 wt. % sodium</td>
<td></td>
</tr>
<tr>
<td>Acetone/water</td>
<td>1/10</td>
</tr>
<tr>
<td>Methanol/water</td>
<td>1/1, 20/1, 3/20</td>
</tr>
<tr>
<td>Water saturated with butyl</td>
<td></td>
</tr>
<tr>
<td>Butyl alcohol saturated with</td>
<td></td>
</tr>
<tr>
<td>water</td>
<td></td>
</tr>
</tbody>
</table>
a) Ethanol-water Polishing

Mixtures of ethanol and water with alcohol water ratios varying from 1/2 to 10/1 were found to yield reasonably good polished surfaces. As the ratio of ethanol to water decreased, the polished surface became even smoother and the rate at which the material is removed also increased. In Fig. A4-7 is shown a crystal polished for one second in an ethanol/water solution at a ratio of 10/1.5. In Figure A4-8 is shown a crystal polished for 60 seconds at an ethanol/water ratio of 10/1. In both cases the polished surface is quite smooth.

There are, however, three major difficulties encountered in using the ethanol-water polish. Small ethanol/water ratio makes it difficult to control the amount of material dissolved. For example, with an ethanol/water ratio of 1/1, only one second of polishing appears to remove all traces of the original etch pattern. Should one be working with a very small thickness of grown crystal, this large amount of dissolution is undesirable. It is also difficult to reproduce the results of such a polish. Normally such reproducability is established by etching a surface, then polishing, then re-etching, then identifying the re-etched pattern with the original pattern. However, if a great deal of the surface is dissolved, the dissolution pattern at the new surface may not be identical to the original surface. If a high ethanol/water ratio is used,
FIGURE A4-7
CRYSTAL POLISHED FOR 1 SEC. IN EtOH-H$_2$O MIXTURE (1:1.5). 288X
(a) before polishing, (b) after polishing

FIGURE A4-8
CRYSTAL POLISHED FOR 60 SEC. IN EtOH-H$_2$O MIXTURE (10:1). 288X
-396-

FIGURE A4-9 (A)
CLEAVED SURFACE ETCHED
FOR 30 SEC. 288X

Vwl

lw

lw

lw

lw

4;w

Ilk
A

101W

i*

IV

FIGURE A4-9 (B)
SAME SURFACE AS 9A AFTER
1 SEC. POLISH IN EtOH-H 2 0
MIXTURE (1:15) AND 60 SEC
RE-ETCH. 288X

FIGURE A4-lo
SAME SURFACE AS IN FIGURE
A4-5A AFTER POLISHING AND
RE-ETCHING. 288X


the crystal must be polished for a long time to obliterate the original etch pattern. However, long polish times seem to increase substantially the number of scratches on the surface; since these scratches etch similarly to low angle boundaries the calculation of the real dislocation density becomes much more difficult. In addition, the latter polishing solution seems to be slightly preferential, consequently a relatively rough surface is left. In addition, the ethanol/water polish solution seems somehow to inactivate the surface for further etching. The normal etch time for a cleaved surface is 30 seconds and gives a pattern shown in Figure A4-9A. In Figure A4-9B, however, the same surface is shown after an ethanol/water polish and a 60 sec. etch. In the latter figure the pits are much smaller and much more dense. Since this was found to be the case in several other trials, it was concluded that some portion of the ethanol/water polishing procedure partially inactivates the surface and makes the ensuing etch much slower and less preferential. The possibility that the butyl alcohol rinse used after the polish was remaining on the crystal was considered; this conjecture was, however, eliminated by baking the crystals (after polishing) for an hour in 110°C oven. The same reduced rate of etching was found.

It was finally discovered that an extended butyl alcohol rinse (on the order of two minutes with agitation)
would eliminate the re-etching problems; however, the extended rinse greatly increases the number of scratches which appeared on the final polished surface.

On those infrequent occasions when re-etching occurred at a normal rate, and when the polished surface was not covered with scratches, the reproducability of the ethyl alcohol/water polish solution was good. In Figure A4-10 shown a crystal surface which has been etched, polished, and re-etched. This original etched surface is shown in Figure A4-5A; it can be seen that there is nearly a one-to-one correspondence between the two patterns, which is satisfactory for our purpose, i.e. calculation of dislocation densities. The two large scratches are typical of those which occur during long rinsing or polishing steps.

b) Lubenets and Kostin's mixture

Lubenets and Kostin published in 1962 a communication to Kristallografiya (118) suggesting the following procedure for polishing potassium chloride crystals. (The times were not listed and those tabulated below were established by a large amount of experimentation as those optimum for the use desired). The crystal is soaked in fuming hydrochloric acid for 60 seconds followed by a washing in an ethyl alcohol and ether mixture (equal volume) for ten seconds. Polishing is accomplished by stirring for from 15 to 16 seconds in a solution consisting of equal parts of ethyl and methyl alcohol, aqueous ammonia,
glycerine, and a saturated solution of barium carbonate in ethyl alcohol. Finally the crystal is carefully washed in dry ethyl alcohol for 15 seconds. In the polishing the original etch step completely disappears after about 15 seconds; the remaining polishing served only to smooth further the surface. Lubenets and Kostin report that this treatment would remove a one or two micron thickness layer of potassium chloride. In this study it was found that this polish was superior to the ethyl alcohol/water solution in that it removed material at a slower rate and it did not appear to retard the rate of re-etching. The problem of causing surface scratches was also considerably reduced using this technique. Reproducibility, however, is only qualitatively good, i.e. a one-to-one correspondence between the re-etched surface and the original surface has not been obtained. However, the over-all pattern remains approximately the same. In Figures A4-11 (A and B) are shown original and etched surfaces; the same lower angle boundaries appear in each but there is not a one-to-one relationship between the original etched pits, and the pits of the re-etched surface. Considering all factors though, this polishing technique does seem to be superior in general to the ethanol alcohol/water polish; probably with some additional refinements, a one-to-one correspondence between the original and re-etched surfaces could be obtained.
Comparison of etched and re-etched surfaces (after polishing). 565X

(a) original etched surface
(b) polished and re-etched surface
A4.2.4 Conclusions

An etching technique has been developed which yields a reliable determination of the dislocation density of potassium chloride crystals. Operating conditions have been determined for the use of methanol saturated with ammonium chloride as an etchant, which gives a one-to-one correspondence between dislocations and etch pits.

Two polishes have been developed for use in the preparation of rough surfaces for etching. Ethanol-water solutions and a complex mixture suggested by Lubenets and Kostin both give good polishing results; the Lubenets-Kostin polish is superior in that it yields a surface which is much easier to re-etch.

A4.3 Application of Etching Technique to Crystals Grown from Solution

A tabulation of all the etch pit density measurements is presented in Table A4-2. For the definition of the term "transition region", see Section 9.2.2. In Figure A4-12 the positions at which the densities were measured are mapped on the cleaved crystal surface. The cleaving procedure is discussed in Section 9.2.2 (see also Figure 9-1). The points from which the pictures of the etched surfaces were taken are also indicated in Table A4-2.

Finally, a part of the area presented in Picture 11 (Figure 9-6) was photographed at a greater magnification and is presented in Figure A4-13.


<table>
<thead>
<tr>
<th>Point</th>
<th>Dislocation Density</th>
<th>cm⁻²</th>
<th>Picture No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>seed region</td>
<td>&quot;transition&quot; region</td>
<td>grown region</td>
</tr>
<tr>
<td>Crystal A-37-1</td>
<td>1.6 x 10⁷</td>
<td>1.7 x 10⁷</td>
<td>1.4 x 10⁷</td>
</tr>
<tr>
<td>1</td>
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<td>1.7 x 10⁷</td>
<td>1.4 x 10⁷</td>
</tr>
<tr>
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<td>1.7 x 10⁷</td>
<td>1.7 x 10⁷</td>
<td>1.4 x 10⁷</td>
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<td>1.7 x 10⁷</td>
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<td>1.0 x 10⁷</td>
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<td>1.0 x 10⁷</td>
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TABLE A4-2
(continued)

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<th>cm⁻²</th>
<th>Picture No.</th>
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</tr>
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<td>1.1 x 10⁷</td>
<td></td>
</tr>
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<td>1.2 x 10⁷</td>
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<td>9 (Figure 9-5)</td>
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<td>2.3 x 10⁷</td>
<td></td>
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<td>7</td>
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<td>2.8 x 10⁷</td>
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<td>5.8 x 10⁶</td>
<td></td>
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<td>5.1 x 10⁶</td>
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<td>2.3 x 10⁷</td>
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<td>11 (Figure 9-6)</td>
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</tr>
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<td></td>
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</tr>
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<td>1.4 x 10⁷</td>
<td>5.1 x 10⁶</td>
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<tr>
<td>6</td>
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<td>5.1 x 10⁶</td>
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<td>5.1 x 10⁶</td>
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<td>5.1 x 10⁶</td>
<td></td>
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<td>1.0 x 10⁷</td>
<td>2.3 x 10⁷</td>
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</tr>
<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5.1 x 10⁶</td>
<td>3.0 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.2 x 10⁷</td>
<td>2.0 x 10⁷</td>
<td>12 (Figure 9-6)</td>
</tr>
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<td>2.7 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>Crystal B-24-1</td>
<td>1.0 x 10⁷</td>
<td>2.4 x 10⁷</td>
<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td>2</td>
<td>2.7 x 10⁷</td>
<td>2.4 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>2.4 x 10⁷</td>
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<td>2.4 x 10⁷</td>
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Table A4-2
(continued)

<table>
<thead>
<tr>
<th>Point</th>
<th>Dislocation Density cm(^{-2})</th>
<th>Picture No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>seed region</td>
<td>&quot;transition&quot; region</td>
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<td>Crystal B-21-2</td>
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<td></td>
</tr>
<tr>
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<td>2.0 x 10(^7)</td>
<td>2.3 x 10(^7)</td>
</tr>
<tr>
<td>2</td>
<td>1.6 x 10(^7)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>8.8 x 10(^6)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.6 x 10(^6)</td>
<td>2.8 x 10(^7)</td>
</tr>
<tr>
<td>5</td>
<td>1.5 x 10(^6)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1.2 x 10(^7)</td>
<td>1.6 x 10(^7)</td>
</tr>
<tr>
<td>7</td>
<td>1.0 x 10(^7)</td>
<td></td>
</tr>
<tr>
<td>Crystal B-24-3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.1 x 10(^7)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>3.0 x 10(^7)</td>
</tr>
<tr>
<td>3</td>
<td>1.4 x 10(^7)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>2.1 x 10(^7)</td>
</tr>
</tbody>
</table>
FIGURE A4-12
AREAS WHERE PIT DENSITY WAS MEASURED

Dotted line indicates the size of the seed. Diameter of the optical field at 1000X = 0.012 cm

0.1 cm
Border between seed and grown region, $\pm 10\mu$
(Calculated from the growth rate measurements)

FIGURE A4-13
ETCHED SURFACE OF CRYSTAL GROWN UNDER IRRADIATION
(NO PbCl$_2$ ADDED)
(Part of Area of Picture 11 in Fig. 9-6)
APPENDIX A5
SPECTROGRAPHIC DETERMINATION OF
IMPURITIES IN KCl

A5.1 Details of the experimental procedure

Additional details are presented to supplement the analytical procedure described in Section 8.1.1.

It was stated in that section that the spectrum lines were registered on a photographic plate. The spectra of the various standards and of the unknowns were photographed under identical conditions. It is very important to control carefully the excitation conditions, the time and nature of exposure, and the conditions of development, since the density of a line varies when these conditions vary. In spite of careful control, it is possible for conditions to change accidentally during the analysis; for instance the arc sometimes tends to wander with the result the light of the source is not focused onto the slit of the dark chamber of the spectrograph.

In order to eliminate the effect of variations in the above factors, the density of an internal standard line was also measured in each sample. The internal standard line is a spectrum line of a material added in a definite concentration to the sample. In the case of lead determination, a known quantity of Bi was added as internal standard into each sample. The ratio of the densities of the two lines, i.e. the analysis line and the internal standard line, is unaffected by exposure conditions.
and development conditions. Thus instead of comparing densities of lines, the above ratios of densities were compared.

Actually, in order to achieve greater precision, the measured densities of lines were converted to intensities of light by means of the characteristic curve of the photographic emulsion. (This is a curve in which the density of the film blackening is plotted against the intensity of the light which caused it). And finally, it was the ratio of intensities of light, (i.e. the intensity corresponding to the analysis line and the intensity corresponding to the internal standard line) for the unknown sample which was compared with the ratios of light intensities of the series of known samples.

A5.2 Impurity content of the crystal seed

Crystal seeds were obtained by cleaving large crystals (10-20 gms) grown from melt. Parts taken from this large crystal were also analyzed spectrographically.

The part of the melt crystal, which was sent together with the samples of Series I* for analysis was taken from the same place in the large crystal from which the seeds for runs B-38 to B-41 had been taken. It should be noted, however, that some of the samples sent for analysis contained crystals grown at earlier dates. The seeds used for those crystals were taken from another part of the large crystal or from other crystals, which were not avail-

*See Section 8-2.
able at the time of analysis.

Three samples of the above mentioned crystal (after the crystal was crushed and homogenized) when analyzed did not show any lead line in the spectrum, which indicated a lead concentration of less than 0.1 parts per million (see Table A5-1, Crystal 1).

It was assumed, therefore, for the calculations in series I determinations, that the seed part contained no lead.

In series II, however, the seeds were obtained from a different melt crystal. Two parts of this crystal were analyzed for Pb, Fe, Bi, Hg. No Bi (<0.5 ppm) or Hg (<10 ppm) were detected. However, both contained Pb and Fe. Each crystal part was crushed separately and three samples were taken from each one for analysis (see Table A5-1, crystals 2 and 3). The values, which were obtained for the Pb and Fe content indicate also that both impurities were non-homogeneously distributed and in such a scale that homogenization could not be attained even after crushing and mixing. (Sanni (145) in his calculations used an average value of 5.8 ppm as the lead content and 65 ppm as the iron content of the seed crystals)

To test further this variation in the impurity content, three more crystals were analyzed. The two (crystals 4 and 5 in Table A5-1) were cleaved from the same large crystal as crystal 1 but from a different part, and the other (crystal 6) was taken from another crystal.
Table A5-1

Lead and Iron Content of Seed Crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Sample 1 Pb ppm</th>
<th>Sample 2 Pb ppm</th>
<th>Sample 3 Pb ppm</th>
<th>Percentage Average Deviation</th>
<th>Sample 1 Fe ppm</th>
<th>Sample 2 Fe ppm</th>
<th>Sample 3 Fe ppm</th>
<th>Percentage Average Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal 1</td>
<td>N.D.*&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>-</td>
<td>not analyzed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal 2</td>
<td>5.8</td>
<td>18.5</td>
<td>7.8</td>
<td>±49%</td>
<td>42</td>
<td>76</td>
<td>78</td>
<td>±24%</td>
</tr>
<tr>
<td>Crystal 3</td>
<td>3.7</td>
<td>3.5</td>
<td>5.2</td>
<td>±17%</td>
<td>28</td>
<td>32</td>
<td>35</td>
<td>±7.7%</td>
</tr>
<tr>
<td>Crystal 4</td>
<td>N.D.*&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>-</td>
<td>8</td>
<td>11</td>
<td>11</td>
<td>±13.5%</td>
</tr>
<tr>
<td>Crystal 5</td>
<td>1.2</td>
<td>1.7</td>
<td>1.7</td>
<td>±14.5%</td>
<td>19</td>
<td>9.8</td>
<td>12.5</td>
<td>±25%</td>
</tr>
<tr>
<td>Crystal 6</td>
<td>5.0</td>
<td>1.7</td>
<td></td>
<td>±49%</td>
<td>43</td>
<td>24</td>
<td></td>
<td>±27%</td>
</tr>
</tbody>
</table>

*N.D. = not detected
Thus the important conclusion is reached that the impurity concentration varies inside the seed crystal. It is possible that in some of the seeds, from which the crystals of series I were grown, the concentration of lead may not be zero as was assumed. If it were not zero, this introduces, of course, an uncertainty which could be responsible for variations observed in the analysis of samples originating from the same crystal. To estimate the effect of the presence of lead in the seed crystals, the lead concentrations of the following three samples were recalculated assuming 5 ppm lead in their seeds.

<table>
<thead>
<tr>
<th>Series I Recalculated Values</th>
<th>Old Values</th>
<th>% Decrease</th>
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<tr>
<td>Sample No 4 196 moles PbCl₂/mole KCl</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>Sample No 7 120</td>
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</tr>
<tr>
<td>Sample No 11 48</td>
<td>52</td>
<td>4</td>
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</table>

This indicates that the error introduced by the lead content of the seed crystal is not high enough to affect at least the magnitude of the calculated value of lead in the grown part.

A5.3 Reliability of the spectrographic method of analysis

The spectrographic method is considered accurate and precise for the determination of lead or iron, especially for concentrations higher than 10 ppm.

To check the precision of the method, two or three determinations were performed from the same homogenized sample. The results are presented in Table A5-2 together with the calculated percentage deviations.
# TABLE A5-2

REPRODUCIBILITY OF Pb AND Fe DETERMINATIONS

## A. Pb Determination

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentrations of Pb ppm</th>
<th>Percentage Deviations</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>53, 55</td>
<td>3.6%</td>
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<tr>
<td></td>
<td>52, 52</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>57, 51</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>110, 90</td>
<td>18</td>
</tr>
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<td></td>
<td>88, 78</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>60, 54</td>
<td>10</td>
</tr>
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<td></td>
<td>113, 115</td>
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</tr>
<tr>
<td></td>
<td>80, 78</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>90, 104</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>90, 100</td>
<td>10</td>
</tr>
<tr>
<td>S-3A*</td>
<td>4.2, 3.5</td>
<td>20</td>
</tr>
<tr>
<td>S-15G</td>
<td>15.3, 14.8, 15.3</td>
<td>3.3</td>
</tr>
<tr>
<td>S-16F</td>
<td>25.5, 28.5</td>
<td>10</td>
</tr>
<tr>
<td>S-10</td>
<td>3.7, 4.8, 5.6</td>
<td>34</td>
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<tr>
<td>S-16D</td>
<td>12.2, 14.0, 14.6</td>
<td>16</td>
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<td>S-16H</td>
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<td><strong>Average Percentage Deviation</strong></td>
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## B. Fe Determination

<table>
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<th>Concentrations of Fe ppm</th>
<th>Percentage Deviations</th>
</tr>
</thead>
<tbody>
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<td>82, 90</td>
<td>9</td>
</tr>
<tr>
<td>S-15G</td>
<td>175, 145, 165</td>
<td>17</td>
</tr>
<tr>
<td>S-16F</td>
<td>96, 94</td>
<td>2.1</td>
</tr>
<tr>
<td>S-10</td>
<td>44, 50, 48</td>
<td>12</td>
</tr>
<tr>
<td>S-3</td>
<td>21.5, 26, 25</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td><strong>Average Percentage Deviation</strong></td>
<td><strong>11.4%</strong></td>
</tr>
</tbody>
</table>

*See Table 8-2
The percentage deviation was expressed as

\[
\left( \frac{\text{maximum value} - \text{minimum value}}{\text{maximum value}} \right) \times 100
\]

The average percentage deviation was for both, the Pb and Fe determinations about 11.5%.

APPENDIX A6

DISTRIBUTION OF LEAD ON THE CRYSTAL SURFACE

Crystals grown from solutions in which no PbCl\(_2\) was added, contained about \(20 \times 10^{-6}\) moles PbCl\(_2\)/mole KCl. In 1 cm\(^2\) of each atomic layer of the (100) planes there are \(5 \times 10^{14}\) molecules of KCl and thereby \(5 \times 10^{14} \times 20 \times 10^{-6} = 1 \times 10^{10}\) atoms Pb/cm\(^2\).

On the other hand, it is deduced from Equation (4-2)

\[
v = v_\infty \left(1 - 2\rho_c d^{1/2}\right)^{1/2}
\]

(4.2)

where 

- \(v\) = the velocity of the step in the presence of an impurity
- \(v_\infty\) = the velocity of the step in the absence of impurities
- \(\rho_c\) = the radius of the two-dimensional critical nucleus
- \(d\) = the density of adsorbed impurities ahead of the step (homogeneous distribution is assumed)

that no growth would occur on a surface in which the density of the homogeneously distributed impurities was higher.
than the density $d$ given by the relation

$$1 - 2\rho_c d^{1/2} = 0 \quad (A6-1)$$

or

$$d = \frac{1}{4\rho_c^2} \quad (A6-2)$$

The value of $\rho_c$ is $5.65 \times 10^{-5}$ cm for a 0.12% supersaturation (see Appendix A8). Therefore $d \approx 8 \times 10^7$ cm$^{-2}$. This permissible density is much lower than the actual density.

Nevertheless growth occurred. The possible explanation* therefore is that the lead ions are not homogeneously distributed; regions probably exist, having a high concentration of lead ions, or even consisting of practically pure PbCl$_2$.

It has been suggested by other investigators (117) that in NaCl containing CaCl$_2$, regions of the latter exist in the form of little plates. This was inferred by x-rays measurements. A similar technique applied to KCl containing PbCl$_2$, would probably elucidate the way PbCl$_2$ is incorporated into the crystals.

*Another possibility is, however, that the value of 46 ergs/cm$^2$ for the interfacial energy, used for the calculation of $\rho_c$, is high. Although, however, it appears to be on the high side, no other value was found in the literature.
APPENDIX A7

CALCULATION OF DIFFUSION COEFFICIENTS
OF LEAD IONS IN POTASSIUM CHLORIDE CRYSTALS

Glassner and Reisfeld (81) have found experimentally that the diffusion coefficient of Pb\textsuperscript{++} in KCl crystals for a temperature range 300-350\,\textdegree\,C is given by the relation:

\[
D_{\text{Pb}^{++}} = 4.41 \times 10^{-3} \exp\left(-\frac{22820}{RT}\right) \text{cm}^2/\text{sec}
\]

The crystallization experiments in this investigation were performed at 35\,\textdegree\,C. The diffusion coefficient of Pb\textsuperscript{++} in KCl at this temperature was found by extrapolation of the above relation. Thus:

\[
D_{\text{Pb}^{++},350\,\textdegree\,C} = 4.41 \times 10^{-3} \exp\left(-\frac{22820}{2 \times 308}\right) = 4.41 \times 10^{-3} \exp(-37) = 3.8 \times 10^{-19} \text{cm}^2/\text{sec}.
\]

APPENDIX A8

CALCULATION OF TWO-DIMENSIONAL CRITICAL NUCLEUS RADIUS

The radius of the two-dimensional critical nucleus is given by the equation (see Section 3.3.2)

\[
\rho_c = \frac{\sigma V_c}{RT \ln(S+1)} \approx \frac{\sigma V_c}{RT S}
\]

(3-32)

where \(\rho_c\) = the radius of the critical nucleus
\(\sigma\) = the interfacial free energy
\(V_c\) = the crystal molar volume
\(S\) = the supersaturation
The value for the interfacial energy obtained by Sears is 46 ergs/cm² (153). It should be noted that this value for KCl crystal in contact with its saturated solution is lower by a factor of two than the surface tension of the fused salt in contact with nitrogen or than the calculated value for solid KCl in contact with its own vapor, as Sears pointed out. It is, therefore, in the right direction.

Thus \( \sigma = 46 \text{ ergs/cm}^2 \)

\[
V_c = 74.55 \text{ gm/mol} \times \frac{1}{1.98} \text{ cm}^3/\text{gr} = 37.8 \text{ cm}^3/\text{mol}
\]

\[
R = 8.31 \times 10^7 \text{ erg/}^\circ\text{K/mol}
\]

\[
T = 308^\circ\text{K}
\]

Therefore

\[
\rho_c = \frac{46 \times 37.8}{8.31 \times 10^7 \times 308 \times S} = \frac{6.8 \times 10^{-8}}{S} \text{ cm}
\]

The following table gives the value of \( \rho_c \) for different supersaturations

<table>
<thead>
<tr>
<th>( \Delta T^* )</th>
<th>( S )</th>
<th>( \rho_c ) cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2°C</td>
<td>0.0012</td>
<td>5.65 \times 10^{-5}</td>
</tr>
<tr>
<td>0.3°C</td>
<td>0.0020</td>
<td>3.40 \times 10^{-5}</td>
</tr>
<tr>
<td>0.7°C</td>
<td>0.0044</td>
<td>1.54 \times 10^{-5}</td>
</tr>
<tr>
<td>0.8°C</td>
<td>0.0051</td>
<td>1.33 \times 10^{-5}</td>
</tr>
</tbody>
</table>

*\( \Delta T \) = the difference between the saturation temperature and the crystallization temperature.

It should be emphasized that the value of \( \sigma = 46 \text{ ergs/cm}^2 \) was deduced by Sears from two-dimensional nucleation correlations of growth rate data. The data, however, were semi-
quantitative and it is possible that it is not quite accurate.

**APPENDIX A9**

**CONCENTRATION OF VACANCIES PRODUCED BY THE EMPLOYED \( \gamma \)-RADIATION DOSE RATE**

**A9.1 Rate of vacancy production**

The employed dose rate was 2400 rad/min (see Appendix A3.5).

**Calculation of flux.** The dose rate is given by (16)

\[
D_\theta^\theta(R) = 5.767 \times 10^{-5} \frac{\mu_a}{\rho} E_0 \phi_\gamma \text{ rads/hr} \quad (A9-1)
\]

where \( E_0 \) = photon energy of radiation source, Mev
\( \frac{\mu_a}{\rho} \) = energy-absorption mass attenuation coefficient, cm\(^2\)/gm
\( \phi_\gamma \) = the photon flux, photons/cm\(^2\)/sec

Substituting the values \( D_\theta^\theta(R) = (2400)(60) \) rads/hr
\( E_0 = 1.25 \) Mev
\( \frac{\mu_a}{\rho}(H_2O) = 0.298 \quad (16) \)

in Equation (A9-1) it is found

\[
\phi_\gamma = \frac{(2400)(60)}{(5.767 \times 10^{-5})(1.25)(0.298)} = 6.7 \times 10^{10} \text{ photons/cm}^2/\text{sec}
\]

or \( 4 \times 10^{12} \) photons/cm\(^2\)/min

**Calculation of displacement cross section**

Nowick (137) has measured the number of displacements produced in NaCl by \( \gamma \)-rays. Twenty minutes irradiation with
a flux \( \phi = 5 \times 10^{12} \) photons/cm\(^2\)/min produced 4 \( \times 10^{16} \)
F-centers.

Therefore from the relation

\[
R_d = \sigma \phi N_0
\]

where \( R_d \) = atoms displaced/cm\(^3\)/min

\( N_0 \) = the number of atoms/cm\(^3\)

it is found that

\[
\sigma = \frac{\frac{4 \times 10^{-16}}{20 \times \frac{1}{5.1 \times 10^{12} \times 4.6 \times 10^{22}}} = 8.7 \times 10^{-21}}{cm^2}
\]

It was assumed that KCl will have a cross section close to this value. For the calculations, the value 8 \( \times 10^{-21} \) cm\(^2\) will be used.

Calculation of the rate of vacancy production

From Equation (A9-1)

\[
R_d = 8 \times 10^{-21} \times 4 \times 10^{12} \times 3.22 \times 10^{22} = 1 \times 10^{15} \text{ displ/cm}^3/\text{min}
\]

A9.2 Calculation of total number of displacements in a growing crystal of KCl

The time it takes for one atomic layer (3\(^0\)A) to be covered is \( t = \frac{3 \times 10^{-8} \text{ cm}}{10^{-2} \text{ cm/hr}} = 3 \times 10^{-6} \text{ hr} = 1.8 \times 10^{-4} \text{ min.}

At any given time the top layer has been irradiated for \( t \) min, while the second layer for 2\( t \) and the Nth (the first deposited) for N\( t \).

The volume of 1 cm\(^2\) of monolayer is \( 1 \text{ cm}^2 \times a = a \text{ cm}^3 \)

where \( a \) is the step height of the crystal lattice. The atoms displaced when N layers have been deposited is
\[ R^*_d = (1 + 2 + \ldots + N) t R_d a = \frac{N(N+1)}{2} t R_d a \]

where \( t, R_d, \) and \( a \) as defined above.

For a potassium chloride crystal \( a = 3 \times 10^{-8} \) cm. The crystals B-10-2 and B-12-1 (see Table 9-1) advanced about only 200 \( \mu \). Therefore \( N = \frac{2 \times 10^{-2}}{3 \times 10^{-8}} = 6.7 \times 10^5 \) and the number of displacements produced in the grown part per \( \text{cm}^2 \) of crystal surface is now

\[
R^*_d = \frac{(6.7)^2 \times 10^{10}}{2} \times 1.8 \times 10^{-4} \times 3 \times 10^{-8} \times 1 \times 10^{15} =
\]

\[ = 1.2 \times 10^{15} \text{ displacements}. \]

**APPENDIX A10**

**APPLICATION OF FROESSLING EQUATION TO CRYSTALS OF KCl, GROWING IN A SUPERSATURATED SOLUTION**

The following equation has been suggested by Froessling (75) to calculate the mass transfer coefficient from or towards a sphere, mounted inside a fluid stream:

\[
k_c = \frac{D_v}{d} \left[ 2 + 0.552 (N_{Re})^{1/2} (N_{Sc})^{1/3} \right] \quad (A10-1)
\]

where \( k_c = \text{mass transfer coefficient, cm/sec} \)

\( d = \text{sphere diameter, cm} \)

\( D_v = \text{diffusion coefficient, cm}^2/\text{sec} \)

\( N_{Re} = \text{sphere Reynolds number,} \frac{dU}{\mu} \)

\( N_{Sc} = \text{Schmidt number,} \frac{\mu}{\rho D_v} \)

\( \mu = \text{viscosity, gm/cm/sec} \)

\( \rho = \text{solution density, gm/cm}^3 \)

\( U = \text{average fluid velocity, cm/sec} \)
For a solution of KCl saturated at 35.2°C, the values of the variables are the following (for crystallization at 35°C):

\[ \rho = 1.19 \text{ gr/cm}^3 \]
\[ \mu = 1.15 \times 10^{-2} \text{ gr/cm/sec} \]
\[ D_v = 2.95 \times 10^{-5} \text{ cm}^2/\text{sec} \text{ (see calculation below)} \]

The average volume of the used seed crystals (Run B-39 as an example) was 2.55 x 10^{-3} cm³. Therefore, the diameter of the equivalent sphere was:

\[ d = 0.17 \text{ cm} \]

The average fluid velocities were calculated by a small Pitot tube for three stirrer speeds:

- 650 rpm \( U = 43 \text{ cm/sec} \)
- 900 \( 49 \)
- 1100 \( 61 \)

**Calculation of diffusion coefficient \( D_v \)**

The diffusion coefficient of potassium chloride in water has been determined experimentally by Gosting (84), as a function of the concentration and at 25°C.

The value of the coefficient was 2.199 x 10^{-5} cm²/sec for the concentration of 3.9 moles KCl/liter, which was the higher concentration he worked with. The concentration of a KCl solution saturated at 35.2°C is 332.3 gm/liter or 4.45 moles/liter. Extrapolating to this value a diffusion
coefficient equal to $2.25 \times 10^{-5}$ cm$^2$/sec is found. This value is for a temperature of $25^\circ$C.

To determine the diffusion coefficient $D_v$ of KCl for the same concentration but at $35^\circ$C, the Onsager-Fuoss equation is used:

$$D_v = 2000RT\left(\frac{M}{C}\right)(1 + C\ln f)$$

(A10-2)

where

$$\frac{M}{C} = 1.074 \times 10^{-20}\frac{\lambda_{K^+} + \lambda_{Cl^-}}{\lambda_{K^+} + \lambda_{Cl^-}} \left(\frac{\lambda_{K^+} - \lambda_{Cl^-}}{\lambda_{K^+} + \lambda_{Cl^-}}\right)^2 2.21 \times 10^{-19} \sqrt{C}$$

(A10-3)

and $\phi(A'\sqrt{C})$ a function, which can be computed from a table given by Harned and Owen (87). The symbols represent the following.

$\lambda_{K^+} = $ equivalent ion conductance of $K^+$

$\lambda_{Cl^-} = $ equivalent ion conductance of $Cl^-$

$\mu = $ the viscosity of water, gr/cm/sec

$\epsilon = $ dielectric constant of the water

$f = $ the mean ion activity concentration

$C = $ the concentration of KCl in the solution, moles/lit

$T = $ the temperature, $^\circ$K

$a^0 = $ ion size parameter, cm.
Gosting used Equation (A10-2) to calculate a theoretical value for the diffusion coefficient $D_v$ at $25^\circ C$. The calculated value is $2.9 \times 10^{-5}$ cm$^2$/sec for the concentration 4.45 moles KCl/lit.

This value is higher than his experimental value of $2.25 \times 10^{-5}$ cm$^2$/sec. Obviously the value which will be found from Equation (A10-2) for $35^\circ C$ is also probably going to be higher than the actual. However, the assumption could be made that the difference between actual and calculated values at $35^\circ C$ is the same as the difference between the same values at $25^\circ C$, i.e. $0.65 \times 10^{-5}$.

The $D_v$, theoretical, $35^\circ C$ can be calculated as follows from Equation (A10-2).

For $25^\circ C$ \[ D_v,\text{theor},25^\circ = 2000R(298.16)(\frac{M}{C})_{25^\circ}(1+\frac{d\ln f}{dC}) \] (A10-5)

and for $35^\circ C$ \[ D_v,\text{theor},35^\circ = 2000R(308.16)(\frac{M}{C})_{35^\circ}(1+\frac{d\ln f}{dC}) \] (A10-6)

Dividing (A10-6) with (A10-5)

\[ \frac{D_v,\text{theor},35^\circ}{D_v,\text{theor},25^\circ} = \frac{(308.16)}{(298.16)} \frac{(M/C)_{35^\circ}}{(M/C)_{25^\circ}} \] (A10-7)

The values of the ratio $M/C$, are obtained from Equation (A10-3), by the use of the values of the following table:
<table>
<thead>
<tr>
<th></th>
<th>Ref.</th>
<th>$T = 298.16^\circ K$</th>
<th>$T = 308.16^\circ K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu, \text{ gm/sec/cm}$</td>
<td>(84)</td>
<td>$8.92 \times 10^{-3}$</td>
<td>$7.21 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>(84)</td>
<td>78.54</td>
<td>75.04</td>
</tr>
<tr>
<td>$\lambda_{k^+}$</td>
<td>(3)</td>
<td>73.50</td>
<td>88.21</td>
</tr>
<tr>
<td>$\lambda_{Cl^-}$</td>
<td>(3)</td>
<td>76.34</td>
<td>92.21</td>
</tr>
<tr>
<td>$C, \text{ mole/lit}$</td>
<td></td>
<td>4.45</td>
<td>4.45</td>
</tr>
<tr>
<td>$A'$</td>
<td></td>
<td>1.15</td>
<td>1.155</td>
</tr>
<tr>
<td>$A'\sqrt{C}$</td>
<td></td>
<td>2.42</td>
<td>2.43</td>
</tr>
<tr>
<td>$\phi(A'\sqrt{C})$</td>
<td>(87)</td>
<td>0.0148</td>
<td>0.0146</td>
</tr>
<tr>
<td>$(\epsilon T)^{1/2}$</td>
<td></td>
<td>$1.528 \times 10^2$</td>
<td>$1.522 \times 10^2$</td>
</tr>
</tbody>
</table>

It was found that $(M/C)_{25^\circ C} = 4.164 \times 10^{-19}$

and $(M/C)_{35^\circ C} = 5.005 \times 10^{-19}$

Substituting in (A10-7), it is found that

$$D_{v, \text{theor}, 35^\circ C} = (2.9 \times 10^{-5}) \frac{308.16}{298.16} \frac{5.005}{4.164} = 3.6 \times 10^{-5}$$

Therefore the actual value of the diffusion coefficient at $35^\circ C$ can be assumed to be

$$D_{v, 35^\circ C} = 3.6 \times 10^{-5} - 0.65 \times 10^{-5} = 2.95 \times 10^{-5}$$

Calculation of Schmidt number

$$N_{Sc} = \left( \frac{\mu}{\rho D_{v, 35^\circ C}} \right) = \frac{1.15 \times 10^{-2}}{1.19 \times 2.95 \times 10^{-5}} = 329$$

and $(N_{Sc})^{1/3} = 6.89$
Calculation of Reynolds numbers

<table>
<thead>
<tr>
<th>$U$, cm/sec</th>
<th>$N_{Re}$</th>
<th>$(N_{Re})^{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>750</td>
<td>27.4</td>
</tr>
<tr>
<td>49</td>
<td>860</td>
<td>29.2</td>
</tr>
<tr>
<td>61</td>
<td>1070</td>
<td>32.6</td>
</tr>
</tbody>
</table>

Calculation of mass transfer coefficients

Applying the above values in Froessling Equation (Equation A10-1) it is found.

For $U = 43$ cm/sec (650 rpm)

\[
k_c = \frac{2.95 \times 10^{-5}}{0.17} \left[ 2 + (0.552)(27.4)(6.89) \right] = 1.84 \times 10^{-2} \text{ cm/sec}
\]

For $U = 49$ cm/sec (900)

\[
k_c = \frac{2.95 \times 10^{-5}}{0.17} \left[ 2 + (0.552)(29.2)(6.89) \right] = 1.96 \times 10^{-2} \text{ cm/sec}
\]

For $U = 61$ cm/sec (1100 rpm)

\[
k_c = \frac{2.95 \times 10^{-5}}{0.17} \left[ 2 + (0.552)(32.6)(6.89) \right] = 2.18 \times 10^{-2} \text{ cm/sec}
\]

Calculation of the corresponding crystal growth rates

Assuming the concentration of the solute at the crystal surface to be the saturation concentration, the corresponding mass transfer rates can be calculated.

For $U = 43$ cm/sec (650 rpm)

$C = \text{solubility at } 35.2^\circ \text{C} = 332.329 \text{ gm/lit}$

$C_s = \text{solubility at } 35^\circ \text{C} = 331.916 \text{ gm/lit}$

$\Delta C = 0.413 \text{ gm/lit} = 5.53 \times 10^{-6} \text{ moles/cm}^3$
Therefore

\[ N_{\text{KCl}} = k_c \Delta c = (1.84 \times 10^{-2})(5.53 \times 10^{-6}) = 1.02 \times 10^{-7} \text{ moles/sec/cm}^2 \]

and the corresponding growth rate of the crystal is

\[ R = 1.02 \times 10^{-7} \text{ moles/sec/cm}^2 \times 74.55 \text{ gm/mole} \times 3600 \text{ sec/hr} \]

\[ = 1.98 \text{ gm/cm}^3 \times 10^{-4} \text{ cm/hr} \]

\[ = 138 \mu \text{hr} \]

Similarly for \( U = 49 \text{ cm/sec} \) (900 rpm), \( R = 147 \mu \text{hr} \)

\( U = 61 \text{ cm/sec} \) (1100 rpm), \( R = 164 \mu \text{hr} \)

Application of Garner and Suckling Equation

It should be emphasized that application of the equation:

\[ k_c = \frac{D_v}{a} \left[ 2 + 0.95(N_{\text{Re}})^{1/2}(N_{\text{Sc}})^{1/3} \right] \]

which has been suggested by Garner and Suckling (78) for spheres inside liquids, would lead to substantially higher values for the mass transfer rate of KCl or crystal growth rate.

For instance, for \( U = 43 \text{ cm/sec} \) (650 rpm), \( R = 232 \mu \text{hr} \).

APPENDIX A1

RE-INTERPRETATION OF DATA REPORTED IN A PREVIOUS PROGRESS REPORT (AEC-TID 19668, Nov. 1963)

It has been concluded in Section 10.2.3 that \( \gamma \)-irradiation did not have any measurable effect on the growth rate of KCl from solutions containing no added PbCl\(_2\).

However, in a previous progress report (AEC-TID 19668, Nov. 1963) it was stated that the data available at that time
indicated an increase in the growth rate inside the radiation field.

This contradiction can be explained as follows: The irradiation runs reported in the previous report were conducted in between runs A-41 and A-42.* At that time, no check experiments without irradiation were performed for each irradiated solution. The data under irradiation were compared with the growth rate measurements in Runs A-20 to A-41. It seems, however, that after run A-41 a change in the impurity content of the reagent grade KCl (Baker Analyzed) took place.

It appears that the new material had less impurities and as a result its solutions were giving higher growth rates. This is evident from Figure All-1. (This plot contains the runs of Figure 7-4, which were conducted with stainless steel shaft and crystal holder - see Section 7.1.3 for the significance of the plotting). All points representing the runs performed after A-41 lie to the left of a curve E (fast growth) and almost all points for runs A-19 to A-41 to the right of the same curve (slow growth).

Therefore, the observed increase in growth rates under irradiation resulted from a coincidental change in the impurity content of the reagent KCl. From then on, the procedure was modified and from each irradiated solution, growth rate data without irradiation were always obtained.

*Both these runs were conducted outside the radiation field.
Figure AII-1: Average Growth Rates of KCl Crystals at Various Supersaturation Levels

- Each point represents a different solution.
- • Runs previous to A-41
- ○ Runs after A-41

See Table 7.3B
APPENDIX A12

INCORPORATION OF Fe+++ in KCl CRYSTALS

The data in Table 8-2 show that crystals S-16F and S3-A both contain the same concentration of iron although only the second was grown from a solution in which Fe+++ had been added. This is not surprising, however, since the reagent is reported to contain as much as $0.6 \times 10^{-6}$ moles Fe/mole KCl. This can probably explain why the added Fe+++ did not affect the growth rate; (see Appendix A15.2) it had been affected already by the iron impurity contained in the reagent.

Therefore the statement that iron is incorporated in large amounts in KCl crystals without affecting their growth can be substantiated only by working with higher concentrations of Fe+++ in the solution.

What, however, can be stated is that although the concentration of Fe+++ at the surface is at least as high as that of Pb++, the latter is much more effective than Fe+++ in retarding the growth. It seems therefore that what is important is not only the concentration of the adsorbed impurity at the surface but the stability of the complexes formed by the impurity at the surface as well as in the bulk of the crystal (i.e. what Bunn calls two- and three-dimensional complexes - see Section 4.3). If the three dimensional complex of Fe+++ is stable, the advancing growth steps incorporates it easily; thus no or very
small resistance is offered to the passage of the step.

The other important piece of information offered by the data in Table 8-2 is that in the presence of Bi$^{+++}$ the concentration of the Fe$^{+++}$ in the crystal increased by a factor of three.

No explanation can be offered at this time. A speculation is based on the fact that Bi$^{+++}$ favors the development of (111) faces on KCl. It is possible that Fe$^{+++}$ adsorbs on this face in considerable amounts.

Nevertheless the above observations indicate that a study of the interaction of the various impurities will be very helpful in illuminating the mechanism of impurity uptake.

**APPENDIX A13**

**EFFECT OF STIRRING ON NUCLEATION - THE ROLE OF THE IMPURITY DIFFUSION RATE**

In 1961 Mullin and Raven (131) pointed out that contrary to what was believed up to that time, an increase in the intensity of agitation did not necessarily lead to a continuous enhancement of the nucleation process. Actually their experiments with solutions of ammonium dihydrogen phosphate, magnesium sulphate and sodium nitrate indicated a region where the tendency to nucleate will start decreasing with an increase in stirring (132). (The actual dependence was similar to Curve C in Figure A13-1).
The critical supercooling, i.e. the difference between saturation temperature and the temperature at which nuclei are first observed, is used there as a measure of the nucleation rate.

The explanation they offered was the following: nucleation is considered to occur by diffusion of solute particles to an embryo (i.e. a sub-critical crystal fragment), followed...
by pseudo-chemical reaction, when the particle joins the lattice. The resultant dependence of the nucleation rate \( J \) on stirring rate may be expressed by an equation of the form:

\[
J \propto (\text{rpm})^n.
\]  

This equation plotted in Figure A13-1 gives a curve of the form of A, in which the critical supercooling decreases - i.e. the nucleation tendency increases - as the stirring rate increases. At the same time, however, it was assumed by Mullin and Raven that a conflicting effect due to attrition of the nuclei is operating. The effect of attrition was attributed to "the fracture of nuclei, either by mutual collision or impact with the vessel, which would yield fragments of less than nuclei size, and thus reduce the net rate at which embryos grow into nuclei", and can be represented by a curve of the form B in Figure A1 -1. Curves A and B are combined to give curve C, which is similar in form to the experimental curve.

However, a different explanation regarding the effect represented by curve B is offered. It is suggested that as the stirring rate increases the amount of impurities diffused to the nuclei surfaces also increases. It has been found by other investigators (18) that impurities can poison the nuclei and increase the critical supercooling. Therefore, an increased stirring rate may increase the
critical supercooling, if impurities are present in the solution.

   Mullin and Raven (132) do not report the purity of the salts they used. However, reagent grades contain enough impurities to make the explanation offered very plausible. For instance, reagent MgSO₄ is reported to contain, among others, 10 ppm heavy metals including lead and 100 ppm manganese; NaNO₃ 3 ppm Pb and 1 ppm Fe; and NH₄H₂PO₄ 2 ppm and 5 ppm Fe.
APPENDIX A14

TA B U L A T I O N  O F  D A T A

Runs with a letter B before their number will be found in Garveito's M.S. Thesis (77)
Runs with a letter A before their number will be found in Saad's M.S. Thesis (45)
Runs A-1 to A-19 and B-1 to B-5 were preliminary

<table>
<thead>
<tr>
<th>Corro. of Added PhCp</th>
<th>Red. Dose</th>
<th>Crystal</th>
<th>Growth in &quot;Units&quot;</th>
<th>Duration</th>
<th>GROWTH RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run moles/dole KC1</td>
<td>rad/min</td>
<td>mm Ho</td>
<td>% Super-</td>
<td>Rate</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>saturation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-20</td>
<td>-</td>
<td>35.0</td>
<td>0.3 ± 0.021</td>
<td>900</td>
<td>1</td>
</tr>
<tr>
<td>A-21</td>
<td>-</td>
<td>35.0</td>
<td>0.3 ± 0.021</td>
<td>800</td>
<td>2</td>
</tr>
<tr>
<td>A-22</td>
<td>-</td>
<td>35.0</td>
<td>0.3 ± 0.021</td>
<td>800</td>
<td>2</td>
</tr>
<tr>
<td>A-23</td>
<td>-</td>
<td>35.0</td>
<td>0.3 ± 0.021</td>
<td>1350</td>
<td>1</td>
</tr>
<tr>
<td>A-24</td>
<td>-</td>
<td>34.93</td>
<td>0.35 ± 0.03</td>
<td>1100</td>
<td>1</td>
</tr>
<tr>
<td>A-25</td>
<td>-</td>
<td>35.0</td>
<td>0.3 ± 0.021</td>
<td>1100</td>
<td>2</td>
</tr>
<tr>
<td>A-26</td>
<td>-</td>
<td>35.0</td>
<td>0.3 ± 0.021</td>
<td>800</td>
<td>2</td>
</tr>
<tr>
<td>A-27</td>
<td>-</td>
<td>35.0</td>
<td>0.3 ± 0.021</td>
<td>800</td>
<td>2</td>
</tr>
<tr>
<td>A-28</td>
<td>-</td>
<td>35.0</td>
<td>0.3 ± 0.021</td>
<td>800</td>
<td>2</td>
</tr>
<tr>
<td>A-29</td>
<td>-</td>
<td>35.0</td>
<td>0.3 ± 0.021</td>
<td>1350</td>
<td>1</td>
</tr>
<tr>
<td>A-30</td>
<td>-</td>
<td>35.0</td>
<td>0.12 ± 0.01</td>
<td>900</td>
<td>1</td>
</tr>
<tr>
<td>A-31</td>
<td>-</td>
<td>35.0</td>
<td>0.4 ± 0.021</td>
<td>900</td>
<td>2</td>
</tr>
<tr>
<td>A-32</td>
<td>-</td>
<td>35.0</td>
<td>0.4 ± 0.021</td>
<td>900</td>
<td>2</td>
</tr>
</tbody>
</table>

**Remarks:**
- "Discontinued" indicates that the run was not completed.
- "Nucleation" indicates that nucleation was observed.
- "Dendritic" indicates that dendritic growth was observed.
- "Incipient dendritic" indicates that dendritic growth was just beginning.
- "Incipient deadritic" indicates that deadritic growth was just beginning.
- "Extensive nucleation" indicates that extensive nucleation was observed.
- "Both solutions A-44 and A-45 from the same stock saturated solution were used." indicates that both solutions A-44 and A-45 were used from the same stock saturated solution.

**Note:**
- The reagent was "Mellin's goot" and not "Baker's analyzed."
<table>
<thead>
<tr>
<th>Run</th>
<th>Conc. of Added Pb/mole KC1</th>
<th>Dose Rate</th>
<th>Temp.</th>
<th>C</th>
<th>OT</th>
<th>Super-</th>
<th>Stirling</th>
<th>Growth in &quot;Units&quot;</th>
<th>Duration</th>
<th>Growth Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-16</td>
<td>1.2 x 10^-7</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>0.8</td>
<td>0.51 ± 0.01</td>
<td>900</td>
<td>18.5</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-17</td>
<td>-</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>0.8</td>
<td>0.12 ± 0.01</td>
<td>900</td>
<td>5.5</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-18</td>
<td>-</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>0.8</td>
<td>0.12 ± 0.01</td>
<td>900</td>
<td>9.3</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-19</td>
<td>-</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>1.1</td>
<td>0.01 ± 0.01</td>
<td>870</td>
<td>2</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-20</td>
<td>-</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>0.8</td>
<td>0.12 ± 0.01</td>
<td>900</td>
<td>7.5</td>
<td>2 hrs.</td>
<td>10</td>
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<tr>
<td>B-21</td>
<td>10^-7</td>
<td>2400</td>
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<td>35.0</td>
<td>0.7</td>
<td>0.12 ± 0.01</td>
<td>900</td>
<td>6</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-22</td>
<td>-</td>
<td>2400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>6</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-23</td>
<td>10^-7</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>0.6</td>
<td>0.38 ± 0.01</td>
<td>900</td>
<td>4.5</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-24</td>
<td>10^-7</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>0.8</td>
<td>0.51 ± 0.01</td>
<td>900</td>
<td>9.5</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-25</td>
<td>10^-7</td>
<td>2400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>11</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-26</td>
<td>10^-7</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>0.4</td>
<td>0.06 ± 0.01</td>
<td>625</td>
<td>4.5</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-27</td>
<td>10^-6</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>2.5</td>
<td>1.60 ± 0.01</td>
<td>900</td>
<td>40</td>
<td>10 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-28</td>
<td>-</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>1.6</td>
<td>0.05 ± 0.01</td>
<td>900</td>
<td>9</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-29</td>
<td>10^-6</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>2.1</td>
<td>1.80 ± 0.01</td>
<td>900</td>
<td>4</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-30</td>
<td>10^-6</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>2.5</td>
<td>1.60 ± 0.01</td>
<td>900</td>
<td>10.5</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-31</td>
<td>10^-6</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>2.5</td>
<td>1.60 ± 0.01</td>
<td>900</td>
<td>20.5</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-32</td>
<td>10^-7</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>0.8</td>
<td>0.21 ± 0.01</td>
<td>790</td>
<td>16</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-33</td>
<td>10^-7</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>0.7</td>
<td>0.44 ± 0.01</td>
<td>790</td>
<td>15</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-34</td>
<td>10^-7</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>0.7</td>
<td>0.44 ± 0.01</td>
<td>950</td>
<td>13</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-35</td>
<td>10^-7</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>0.8</td>
<td>0.51 ± 0.01</td>
<td>900</td>
<td>10.5</td>
<td>2 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-36</td>
<td>0.75 x 10^-7</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>0.75</td>
<td>0.48 ± 0.01</td>
<td>900</td>
<td>2.5</td>
<td>5 hrs.</td>
<td>10</td>
</tr>
<tr>
<td>B-37</td>
<td>10^-7</td>
<td>2400</td>
<td></td>
<td>35.0</td>
<td>0.75</td>
<td>0.48 ± 0.01</td>
<td>1000</td>
<td>2.5</td>
<td>5 hrs.</td>
<td>10</td>
</tr>
</tbody>
</table>

The resistance thermocouple with the only purpose to grow crystals for the spectrographic analysis. The resistance thermocouple was out of order and the temperature in the crystallizer was not recorded.
<table>
<thead>
<tr>
<th>Conc. of Added PbCl₂</th>
<th>Red. Dose Rate</th>
<th>Crystallographic Data</th>
<th>% Supersaturation</th>
<th>Stirring Rate</th>
<th>Crystal Growth in &quot;Units&quot;</th>
<th>Duration of Growth</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run</td>
<td>Run Rate/m³</td>
<td>Temp °C</td>
<td>temp °C</td>
<td>% temp</td>
<td>Crystallization run</td>
<td>No.</td>
<td>L</td>
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<tr>
<td>B-38</td>
<td>10⁻⁷</td>
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<td>35.0</td>
<td>0.8</td>
<td>0.51 ± 0.01</td>
<td>3500</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>B-39</td>
<td>10⁻⁷</td>
<td>0</td>
<td>35.0</td>
<td>0.2</td>
<td>0.12 ± 0.01</td>
<td>860</td>
<td>1</td>
</tr>
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<td></td>
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</tr>
<tr>
<td>B-40</td>
<td>10⁻⁷</td>
<td>0</td>
<td>35.0</td>
<td>0.8</td>
<td>0.51 ± 0.01</td>
<td>850</td>
<td>1</td>
</tr>
<tr>
<td></td>
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<td></td>
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</tr>
<tr>
<td>B-41</td>
<td>10⁻⁷</td>
<td>0</td>
<td>35.3</td>
<td>0.5</td>
<td>0.32 ± 0.01</td>
<td>850</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-42</td>
<td>10⁻⁷</td>
<td>0</td>
<td>35.1</td>
<td>0.7</td>
<td>0.44 ± 0.02</td>
<td>1100</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX A15

SIDE INVESTIGATIONS

A15.1 Flow recycling apparatus

In the investigation summarized below a different apparatus was used than the one described in Chapter 6. The apparatus was constructed by Mr. C. Natsis, a Graduate Research Assistant on the project.

A flow flask (Figure A15-1), was made from a one-liter pyrex flask with a circulation inlet of one inch at the bottom leading to a U shape tube with a return outlet fused at the upper part of the flask. An extension of the vertical portion of the tube led to a one inch tappered joint mouth where a well-fitted teflon stopper was used to support the crystal holder. Teflon stoppers with one, three or seven holes for support of equal number of crystals were made.

At the top of the flask, another larger three-inch diameter, tappered joint mouth was plugged with a one inch thick well-fitted teflon stopper. This stopper had been machined to receive at the top center, in tight fit, a ball bearing through which a stainless steel rod could be passed.

At the end of the rod, three stainless steel blades were pinned down symmetrically (120°) and at a 45° angle with respect to the axis of the rod. These three blades constituted a fan-type impeller which upon rotation via a D-C motor with a controlled voltage input, provided the necessary control of flow in the tube and mixing of the solution in the flask.
Rotation

Ball Bearing
Teflon Stopper

Fan Type Impeller

Crystal Holder

Crystal

FIGURE A15-1
The advantageous features of this setup are: better control of the flow around the crystal, higher liquid velocities are attainable and a large number of crystals can grow simultaneously.

A15.2 Effect of ionic impurities on the growth rate of (100) faces of KCl

The experiments in this part of the investigation were performed by S.A. Sanni, a graduate student at the Department of Chemical Engineering, MIT and are reported in detail in his S.M. thesis (145).

The objective of this part of the investigation was to study the order of effectiveness of the following ionic impurities - Ti^{+++}, Fe^{+++}, Cd^{++}, Sn^{++}, Hg^{++}, Bi^{+++}, Pb^{++}, UO_{2}^{++}, and Th^{++++} on the absolute growth rate of the (100) faces of KCl crystals grown from aqueous solution. Previous investigators have reported only the effect on habit (relative growth rates). The measured variable was the minimum value of supersaturation at which dendritic growth was obtained for each impurity concentration.

The data are summarized in Table A15-1.
**TABLE A15-1**

Minimum Supersaturations at which Dendritic Growth Occurred in KCl for Different Impurities

<table>
<thead>
<tr>
<th>Concentration of added impurities moles/mole KCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>Pb$^{++}$</td>
</tr>
<tr>
<td>Th$^{++++}$</td>
</tr>
<tr>
<td>UO$_2$$^{++}$</td>
</tr>
<tr>
<td>Bi$^{+++}$</td>
</tr>
<tr>
<td>Hg$^{++}$</td>
</tr>
<tr>
<td>Sn$^{++}$</td>
</tr>
<tr>
<td>Fe$^{++}$</td>
</tr>
<tr>
<td>Cd$^{++}$</td>
</tr>
<tr>
<td>Ti$^{+++}$</td>
</tr>
</tbody>
</table>

The order in the table indicates the order of effectiveness. It is observed that Fe$^{+++}$, Cd$^{++}$ and Ti$^{+++}$ showed no effect.

It is suspected, however, that the effect of some of the impurities has been underestimated for two possible reasons.

1) The acidity of the solutions was not enough to prevent hydrolysis of some of the impurities. Only one or two drops were used.

2) The liquid velocity around the crystal was too low (about 16 cm/sec). It is possible that the mass transfer of the impurity was the controlling rate.
A15.3 Dissolution rates of γ-irradiated crystals of KCl

In this part of the investigation the rate of dissolution of γ-irradiated KCl crystals in slightly undersaturated KCl aqueous solutions was investigated experimentally. The crystals were irradiated prior to the dissolution for one-half, one, two, four and thirteen hours in a Co\(^{60}\) source delivering 2400 rad/min. The rates were compared with the dissolution rates of non-irradiated crystals, dissolved in the same mother solution.

The work was performed by Mr. C. Natsis, a graduate Research Assistant in the Department of Chemical Engineering, MIT (May 1964). The research notebook with the detailed data is in the possession of Prof. Robert C. Reid, MIT Department of Chemical Engineering.

In Table A15-2, a summary of the data is presented. Each dissolution rate represents the average of the dissolution rates of three crystals. Each group of crystals consisted of three irradiated and three non-irradiated crystals dissolving simultaneously in the same undersaturated solution.

No significant effect of irradiation or trend was observed. Savinstev et al (147) have reported a higher dissolution rate for irradiated crystals of NaCl (with comparable irradiation doses). However, they actually measured the overall mass dissolution rate of the crystal and not the dissolution rate of the (100) faces as in the present investigation.
TABLE A15-2

Dissolution Rates of (100) KCl Faces for \(\gamma\)-irradiated and Non-irradiated Crystals

(Radiation Dose Rate 2400 rad/min)

<table>
<thead>
<tr>
<th>Group of Crystals</th>
<th>Undersaturation</th>
<th>Irradiation Time, hrs</th>
<th>Rate, (\mu/min) Irradiated Crystals</th>
<th>Rate, (\mu/min) Non-Irradiated Crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.36%</td>
<td>0.5</td>
<td>11.1±1.2</td>
<td>10.3±1.2</td>
</tr>
<tr>
<td>2</td>
<td>0.36%</td>
<td>0.5</td>
<td>10.3±1.8</td>
<td>10.5±1.8</td>
</tr>
<tr>
<td>3</td>
<td>0.36%</td>
<td>1</td>
<td>9.3±1.2</td>
<td>9.9±1.2</td>
</tr>
<tr>
<td>4</td>
<td>0.32%</td>
<td>2</td>
<td>9.6±1.8</td>
<td>9.0±1.8</td>
</tr>
<tr>
<td>5</td>
<td>0.36%</td>
<td>4</td>
<td>13.3±1.8</td>
<td>12.8±1.8</td>
</tr>
<tr>
<td>6</td>
<td>0.32%</td>
<td>13</td>
<td>10.9±1.8</td>
<td>10.6±1.8</td>
</tr>
</tbody>
</table>

It is possible that irradiation affects the dissolution rates of faces other than the (100).

In addition in Savintev's experiments the velocity of the solution passing the crystal was 4 m/sec, while in the experiments of Table A15-2 the corresponding velocity was between 40-50 cm/sec. It is suspected that the dissolution in the latter experiments was mass transfer controlled.
APPENDIX A16

EFFECT OF $\gamma$-IRRADIATION ON THE GROWTH OF
SUCCHINIC ACID CRYSTALS

A16.1 Effect of $\gamma$-irradiation on the nucleation of succinic acid crystals

$\gamma$-Irradiation was found to decrease the degree of supersaturation required to cause nucleation of both pure aqueous solutions of succinic acid and of solutions containing a surface active agent.

More details are given in a previous report (120).

A16.2 Effect of $\gamma$-irradiation on the rate of growth of succinic acid crystals

A series of experiments were performed to test whether $\gamma$-irradiation has any effect on the growth rate of succinic acid crystals.

The procedure followed was identical to the one used for the KCl crystals (see Chapter 10).

The supersaturation varied from 6.8% to 10%.

Comparisons between growth rates with and without irradiation showed that $\gamma$-irradiation had no measurable effect on the growth rate of succinic acid crystal.

Details are given in S.A. Sanni's, S,B, Thesis, MIT, 1964.
SUGGESTED WORK - USE OF IRRADIATION FOR THE STUDY OF WHISKER CRYSTAL GROWTH

Crystals growing in the form of whiskers have been the subject of both experimental and theoretical investigations. (13) Many theories have been proposed to explain their growth, but the reasons for the whiskerlike profile are not yet completely understood.

High energy radiation could be helpful in elucidating the mechanism of whisker growth. Moreover by observing the effects of radiation on a simple system like a whisker, it will enable one to interpret more clearly the already observed effect of irradiation on the rate of growth of a normal crystal. A brief presentation of whisker growth mechanisms will show how and where irradiation could be helpful.

It is generally believed that whisker growth probably starts by winding up a spiral dislocation (64, 72, 136, 150) although some investigators have stated there is no reliable information on the presence or absence of screw dislocations in their whiskers (83, 93). The evidence for the existence of screw dislocations in whiskers has been presented by many investigators, for example Amelinckx (2), who used decoration and etching techniques and Webb et al (176) who used an x-ray diffraction method to observe an elastic twisting of the crystal lattice around a screw dislocation. Matthai and Syrbe (122), on the other hand, tried to induce screw dislocations
in the following way. Starting from the well known observation that pure paraffin crystals grown from solution have growth spirals on the surface, they coated the inside of a Petri dish with molten paraffin, and then poured in an aqueous solution of NaCl, KCl or KBr. The water was allowed to evaporate slowly. When almost all the water was gone they turned over some of the cubic crystals. Whiskers grew on the turned side but they did not grow on the "unturned" crystals. However this cannot be a convincing way of creating dislocations. For instance, there is no reason for expecting that paraffin when quickly cooled will form growth spirals on its surface or that the steps, if they exist, will have any relation to the lattice spacing of NaCl or KCl. Similar experiments, however, could be designed in which radiation could be used to produce dislocations.

There are two observations of whisker growth which were attributed to the acceleration of the whisker growth by irradiation, both however deal with "proper" whiskers, i.e. those which grow from the solid without the atoms which form the whisker passing through another phase. Arnold (6) exposed tin plated specimens to neutron bombardment and at the end of a year, a dense growth of whiskers had occurred, while control specimens which had not been irradiated showed very little growth. Barss et al (7) also observed coarse whiskers growing from the broken ends of a uranium fuel element.
It should be emphasized that screw dislocations provide the necessary but not the sufficient conditions for whisker growth. An important additional point remaining to be answered is why the sides of the whisker do not grow at an appreciable rate. The answers given up to date by many investigators suggest that modifications of growth by impurities, together with the existence of the screw dislocation provide a possible mechanism for inhibiting growth on the four cubic faces while allowing growth to continue on a crystallographic equivalent face. More specifically one of the investigations reported by Amelinckx (2) will be discussed below.

Amelinckx grew crystals of NaCl, KCl, LiF and KBr from a solution containing small quantities of polyvinyl alcohol as a "poison". The crystals grew in a form shown below.
The whiskers were oriented in the six cube directions and they were bounded by cubic faces. Many whiskers had further side branches. Amelinckx explains the role of the impurity in the following way: At the start, a small cubic crystal is formed containing a number of dislocations which emerge as growth spirals. Impurities are adsorbed preferentially along the spiral steps while successive steps emitted by the center will pile up behind the "poisoned" step forming in this way a small terrace, growing at its top face. In other words the concentration of impurity on the newly-formed tip does not reach a high enough value to stop growth at this point. Amelinckx made some remarkable observations by revealing the dislocations in the whiskers by using a decoration technique and an etching technique. The etchant he used worked very well for NaCl but was not as satisfactory for KCl. He was able to observe an axial dislocation of a whisker which branched during growth and produced a side whisker branch. He also postulated "that some of the dislocations which originally emerged in the base will not follow the direction of the whisker axis and will finally emerge in a side face and may give rise to growth there, if they emerge with a screw component".

It should be noted that in the above case the dislocations of the side branches were generated accidentally. A means for controlled generation of dislocations on the side faces of the whisker would obviously be desirable and very helpful in the study of whisker crystal growth.
It is proposed to use high energy radiation (preferably neutrons) for this purpose. More specifically it is proposed to grow crystals of potassium chloride carrying whiskers by the use of the Amelinckx technique. These crystals could be grown with and without irradiation. In one modification the crystals could be grown without irradiation and after the primary whisker branches were developed, the whisker would be subjected to high energy radiation. A correlation of whisker morphology with the dislocations would, hopefully, follow. Potassium chloride would be considered first for the following reason. It has been shown by Amelinckx that under controlled conditions whiskers can be grown on KCl crystals.

Amelinckx suggested in the same article that branching of dislocations may be a process partly responsible for dendritic growth from solution. If this is true we will be able, by irradiating a crystal carrying whiskers, to observe its development to a dendrite and subsequently probably to a filled-in crystal.

Generally, we can then conclude, that the proposed investigation could throw light to the mechanism of whisker crystal growth. In addition the results of this study could have implications concerning the over-all mechanism of crystal growth.

APPENDIX A18
LOCATION OF ORIGINAL DATA
The original copies of the research notebooks are in the possession of Professor Robert C. Reid, M.I.T., Department of Chemical Engineering.
### APPENDIX A19

**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>height of a monatomic growth step</td>
</tr>
<tr>
<td>(a^0)</td>
<td>ion size parameter (Equation A10-4)</td>
</tr>
<tr>
<td>(c)</td>
<td>the velocity of light</td>
</tr>
<tr>
<td>(C_o)</td>
<td>equilibrium concentration of the solute (Chapter 3)</td>
</tr>
<tr>
<td>(C_o^0)</td>
<td>equilibrium concentration of an incorporated impurity in a crystal bulk (Chapters 1, 4, 8)</td>
</tr>
<tr>
<td>(C_1)</td>
<td>concentration of the solute at the surface (Equation 3-3)</td>
</tr>
<tr>
<td>(C_2)</td>
<td>concentration of the solute in the solution (Equation 3-1)</td>
</tr>
<tr>
<td>(C_L)</td>
<td>concentration of a solute (i.e., crystallizing species or impurity) in the mother solution</td>
</tr>
<tr>
<td>(C_{oL})</td>
<td>equilibrium concentration of a solute in the solution</td>
</tr>
<tr>
<td>(C_s)</td>
<td>surface impurity concentration</td>
</tr>
<tr>
<td>(C_{oS})</td>
<td>equilibrium surface impurity concentration</td>
</tr>
<tr>
<td>(C_V)</td>
<td>atomic fraction of vacancies in a crystal lattice</td>
</tr>
<tr>
<td>(d)</td>
<td>density of adsorbed impurities on a crystal surface (Chapter 4)</td>
</tr>
<tr>
<td>(D)</td>
<td>distribution coefficient of an impurity (See Equation 4-27)</td>
</tr>
<tr>
<td>(D_{a(s)})</td>
<td>surface diffusion coefficient of an adsorbed solute atom</td>
</tr>
<tr>
<td>(D_1)</td>
<td>diffusion coefficient of an impurity in a crystal</td>
</tr>
<tr>
<td>(D_{Pb^{++}})</td>
<td>diffusion coefficient of lead ions in the KCL crystal</td>
</tr>
<tr>
<td>(D_V)</td>
<td>diffusion coefficient in the liquid</td>
</tr>
<tr>
<td>(D_{v(s)})</td>
<td>surface diffusion coefficient of a vacancy</td>
</tr>
</tbody>
</table>
the energy of the electron in the Compton process

threshold energy of displacement (Chapters 5,9,10)

energy of desorption (Chapter 3)

electron energy

activation energy for migration of a vacancy

energy transferred to an atom by an electron during collision

energy of formation of a vacancy in a lattice

energy of formation of a vacancy in the crystal surface

the energy of a photon

thickness of a deposited crystal layer

height of a crystal (Figure 6-2)

crystal nuclei formed per unit time and unit area

impurity flux to a growing surface

density of steps on a crystal surface (Eq. 3-42)

- Boltzmann constant
- mass transfer coefficient
- distribution coefficient of an impurity (crystal bulk-to-solution)

equilibrium distribution coefficient of an impurity

"coefficient of crystallization velocity"

effective distribution coefficient of an impurity

surface distribution coefficient of an impurity (crystal surface-to-solution)

length of a crystal (Figure 6-2)

atomic or molecular mass

the rest mass of an electron

concentration of adsorbed solute atoms at the crystal surface
\( n_c \) concentration of critical nuclei
\( n_v \) concentration of vacancies in a crystal
\( n_v^{(s)} \) surface concentration of vacancies
\( N, N_O \) the number of ionic sites in a crystal (per cm\(^3\))
\( N_s \) the number of ionic sites on a crystal surface (per cm\(^2\))
\( q \) the flux of steps (number of growth steps passing a point on a crystal surface per unit time)
\( r_0 \) "classical radius" of the electron
\( R \) growth rate normal to a face (length of face advance per unit time)
\( R_d \) total number of ions displaced in an irradiated crystal (per unit volume and time)
\( S \) surface area of a crystal (Equation 3-1)
\( t \) time
\( U \) liquid velocity
\( v \) velocity (rate of advance) of a step
\( v_\infty \) velocity (rate of advance) of a straight step
\( V_C \) crystal molar volume
\( w \) energy required to form a kink
\( w_{1} \) adsorption energy of an impurity at a kink
\( w_{1}^e \) adsorption energy of an impurity at the edge of a step
\( Z \) atomic number

Greek Letters

\( \delta \) liquid film thickness
\( \varepsilon \) - dielectric constant of water (Appendix A10)
- the ratio \( E_c/E_\gamma \) (Chapter 5)

\( \lambda \) - distribution coefficient of an impurity (See Equation 4-28)

\( \lambda_0 \) - mean distance between kinks in a pure step

\( \lambda_c \) - mean distance between kinks in a poisoned step

\( \lambda_r \) - mean displacement of an adsorbed atom

\( \lambda_{K^+}, \lambda_{Cl^-} \) - equivalent ion conductance of \( K^+ \) and \( Cl^- \) ions

\( \mu \) - solution viscosity

\( \nu \) - frequency factor

\( \xi \) - a factor given in Equation 4-11

\( \xi_c \) - the \( \xi \) factor for crystals grown in a solution

\( \rho \) - radius of a crystal nucleus
- radius of the curvature of a step
- solution density (Equation 7-1 and Appendix A10)

\( \rho_c \) - radius of a critical two-dimensional nucleus

\( \sigma \) - interfacial free energy

\( \sigma_c \) - Compton cross section per unit energy (see Eq. 5-3)

\( \sigma_d \) - displacement cross section (see Eq. 5-4)

\( \sigma_{c,d} \) - displacement cross section of the \( \gamma \)-rays due to the Compton process

\( \sigma(E_\gamma, E_p) \) - collision cross section (see Eq. 5-4)

\( \tau \) - mean life of an adsorbed atom on the surface

\( \phi_\gamma \) - \( \gamma \)-ray flux

\( \omega \) - angular velocity of a growth spiral

\( \Omega \) - volume of a molecule of the solute
Glossary of Terms

Supersaturation  ---  the ratio \( S = \frac{C_L - C^0}{C^0} \)

Percent supersaturation  ---  \(-S \times 100\)

Distribution coefficient  ---  The ratio of the molar fraction impurity-solute in the crystal over the same fraction in the mother solution.
APPENDIX A20

LITERATURE CITATIONS


15. Ibid., p. 13.


26. Ibid., pp. 115-118.

27. Ibid., pp. 147-168.


29. Ibid., p. 362.

30. Ibid., p. 416.


32. Ibid., p. 67.

33. Ibid., p. 72.
34. Ibid., p. 182.
35. Ibid., p. 260.
36. Ibid., p. 407.
37. Ibid., p. 429.
45. Ibid., p. 10.
51. Chlopin, V. et al., Z. anorg. allgem, Chem. 172, 310 (1928).


57. Ibid., p. 117.

58. Ibid., p. 57.

59. Ibid., p. 41.


71. Frank, F. C., Advances in Physics 1, 91 (1952).

72. Frank, F. C., Phil. Mag. 44, 854 (1953).


75. Froessling, N., Gerland's Beit. zur Geophys. 52, 170 (1938).


88. Ibid., p. 161.


105. Klick, C. C., Phys. Rev. 120, 760 (1960).


110. Kossel, W. in Falkenhagen Quantentheorie and Chemie, Leipsig (1928).


164. Ibid., p. 115.
