

Nucleation of Crystals
from Solutions

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by

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Abstract

The formation of nuclei in solutions, due to the presence of a seed crystal, has been studied. This phenomenon has been called "breeding" in order to differentiate it from the more commonly studied nucleation phenomena. Breeding in three solutions was studied: zinc-mercury, aqueous KBr, and aqueous $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Three breeding mechanisms were found:

1) Attrition

Collisions between crystals and either themselves or the vessel walls cause the production of nuclei, probably by the breaking off of small crystal particles from the seed.

2) True Breeding

At relatively high supercoolings, irregular growths in the form of dendrites or needles may form. If the solution is then agitated these may be broken off to form nuclei.

3) Splintering

When irregular growths break off from a seed crystal, a great many nuclei, in the form of crystal splinters, may be produced by the fracture.

In the case of agitated aqueous $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solutions, a particular form of true breeding has been found, in which the irregular growths responsible for breeding occur in the

[001] direction when growth is partly under the influence of diffusion. This mechanism, along with that of attrition, explains the results of Ting and McCabe (1934) on $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solutions.

Of the mechanisms described above, attrition is probably of the greatest practical importance, since it has been seen to occur at very low supercoolings. Showers of crystals were sometimes observed on introducing crystals into still supercooled solutions, but this was felt to be due to the introduction of nuclei with the seed, and is a trivial phenomenon. If all these mechanisms are considered, an explanation is available for most of the very few observations of breeding to be found in the literature.

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Chapter I

INTRODUCTION

When a crystal is added to a supersaturated solution under certain conditions, not only does growth occur, but sometimes new crystals are observed to form. This nucleation phenomenon has been termed "breeding" in order to distinguish it from other types of nucleation, which do not require the presence of a seed, or parent, crystal.

Breeding has been recognized by McCabe¹ as being "probably the most important single method" of production of new nuclei in crystallizers, yet it has never been thoroughly investigated.² In fact, references to the phenomenon in the literature are quite rare. Recently, however, L. Benjamin³, working in the laboratory of Dr. Strickland-Constable, observed breeding when stirred supersaturated zinc amalgams were seeded with a few zinc crystals. The present work is a continuation of the study of breeding in zinc amalgams, and a further investigation of the phenomenon in aqueous solutions of potassium bromide and magnesium sulphate heptahydrate.

Some of the principal observations made during this work can be summarized as follows:

a) When a single fresh crystal is added to a supersaturated solution, a shower of new crystals often appears immediately, apparently caused by the presence of small crystal particles on the seed.

b) If the crystal is then allowed to continue growing in the solution at a sufficiently high supersaturation, and with stirring, occasional new crystals are produced from time to time. These appear to result from the breaking off of needle-like growths. ("True Breeding.")

c) When these needle-like growths break off a further shower of crystals is often produced by the act of fracture. ("Splintering")

d) If crystals are allowed to collide either with each other or the walls in a supersaturated solution, new crystals are very easily produced. ("Attrition.") In b) above, the crystal was considered to be held in such a way as to avoid collision with the walls or with any other crystals. "True Breeding" (type b) is in some ways the most interesting of these categories.

A short discussion of nucleation and crystal growth will precede a review of the known references to the breeding phenomenon.

I - NUCLEATION

The phenomena of supersaturation and the spontaneous nucleation of crystals have been studied for over two hundred years, having been observed by Fahrenheit in 1724. In 1891 Ostwald⁴ introduced the term "metastable" to describe a solution which was supercooled, but insufficiently so to cause spontaneous nucleation. The occurrence of crystallization on further cooling was said to be due to the solution entering into the "labile" state.

These ideas were supported by Miers and his followers, who found that for a variety of substances (and mixtures of substances) well defined curves, roughly parallel to the solubility curves, could be

drawn representing the transition from the metastable to the labile states. These curves were called supersolubility curves, and were quite often closely reproducible.

It is now recognized that the metastable limit is not rigid, as was thought, but represents the region where the probability of a change of phase becomes observable. Nevertheless, the terms used by Ostwald are often used as descriptive terms in modern theories.

Recognition that there was a gradual change from the supersaturated to the labile states followed from the experiments of Tammann⁵ and others, and the theoretical work of Gibbs.⁶ An early calculation of a dependency of nucleation frequency on supersaturation was due to Volmer and Weber⁷, who considered the homogeneous condensation of a drop of liquid from its vapour. Becker and Doring⁸, using this same model and assuming steady state conditions, calculated the rate of nucleus formation to be of the form

$$\begin{aligned} I &= \left[B \exp. -\frac{\Delta G}{kT} \right] \dots\dots\dots (1) \\ &= \left[B \exp. -\frac{16 \pi \sigma^3}{3(kT)^3 (\ln S)^2} \right] \end{aligned}$$

This equation is similar in form to the Arrhenius equation, with B representing a frequency factor and ΔG the free energy of nucleus formation (i.e. the work required to form a nucleus).

Turnbull and Fisher have modified this equation for nucleus formation from liquids, and applied transition state theory to the evaluation of the frequency factor. By making an assumption about the approximate size of the critical nucleus, they obtained the

approximate equation,

$$I \approx \frac{NkT}{h} \exp. \left[\frac{-(\Delta G + \Delta g)}{kT} \right] \dots\dots\dots (2)$$

Δg being the activation energy for diffusion. For homogeneous nucleation in supercooled liquid metals, Holloman and Turnbull¹⁰ have proposed that the work of nucleus formation is given by

$$\Delta G = \frac{16 \pi T_s^2 \sigma^3}{3(\Delta H)^2 (\Delta T)^2}$$

The rate of nucleus formation in liquids therefore becomes:

$$I \approx \frac{NkT}{h} \exp. \left[-\frac{16 \pi T_s^2 \sigma^3}{3(\Delta H)^2 kT (\Delta T)^2} \right] \exp. \left[-\frac{\Delta g}{kT} \right] \dots (3)$$

This equation illustrates the very critical dependance of the nucleation rate on supercooling. It can be applied to solutions by multiplying the pre-exponential term by the mole fraction of solute, and using the appropriate values for ΔH and Δg .

Kuhrt¹¹ has criticized the classical nucleation theory outlined above on the ground that the calculation of the work of nucleation is completely incorrect. If this is so then it can be assumed that any agreement of the Holloman-Turnbull theory with experiment must be regarded as either fortuitous or the result of the adjustment of the pre-exponential factor on the basis of known nucleus sizes. A more general defect of the classical approach to nucleation is the need to apply macroscopically determined values of the interfacial free energy, σ , to submicroscopic nuclei. Another difficulty has been the need to assume that the nucleus is homogeneous and of a

specific size - given by

$$r^* = \frac{2 \sigma V_m}{k T \ln S} \dots\dots\dots (4)$$

A brief reference will therefore be made to the recent theory of Cahn and Hilliard¹², which avoids this assumption. At low supercoolings, the properties of their nucleus approach those of the classical nucleus, but at higher supercoolings the work required for its formation becomes progressively less than that for the classical nucleus, approaching zero at the metastable limit. At the same time, the interface between the nucleus and the exterior phase becomes less definite, until eventually no portion of the nucleus is even approximately homogeneous; the composition at the centre of this "nucleus" approaches that of the exterior phase. With increasing supercooling the radius and excess concentration in the nucleus at first decrease, then pass through a minimum, and finally become infinite at the metastable limit.

The main interest in spontaneous nucleation so far as the present work is concerned, has been in ensuring that it did not occur. In the cases of the aqueous solutions, it was sufficient to determine that agitation equivalent to the maximum encountered experimentally did not cause nucleation. In the zinc amalgams, homogeneous nucleation was encountered at low supersaturations, and the classical theory in the form developed by Turnbull has been applied.

II - CRYSTAL GROWTH

In processes involving the transfer of mass or heat across phase boundaries, it is frequently found that the resistance to the mass or heat transfer is of two kinds: diffusional, involving the rate at which material or heat arrive at the surface of the boundary, and the resistance inherent in the surface reaction process itself. In the case of crystal growth, early work was on the assumption that growth was diffusion controlled, governed by an equation of the type

$$\frac{dm}{dt} = K_D A (S - 1) \dots\dots\dots (5)$$

When the supersaturation is defined as

$$S = \frac{\text{mass fraction of solution, temp. } T}{\text{mass fraction of a saturated solution, temp. } T}$$

the mass transfer coefficient, K_D , has the units of grams / cm² sec.

Where the linear rate of growth is required, the equation corresponding to (5) is

$$\frac{dl}{dt} = \frac{K_D}{\rho} (S - 1),$$

ρ being the density of the crystal.

It was soon recognized that this simple expression was not sufficient, and the theory was modified to take account of a surface reaction following the law

$$\frac{dm}{dt} = K_R A (S_1 - 1)^n \dots\dots\dots (6)$$

where S_1 is the supersaturation at the crystal surface and n may

be considered as the order of the surface reaction. It is possible to eliminate S_i (which is difficult to measure) from these equations, and for a first order surface reaction, combining (5) and (6) yields the relation

$$\frac{dm}{dt} = \frac{A}{\frac{1}{K_R} + \frac{1}{K_D}} (S - 1) \dots\dots\dots (7)$$

When $K_R \gg K_D$, diffusion controls and equation (7) is the same as equation (5). When $K_D \gg K_R$, the surface reaction controls and $S_i \longrightarrow S$ so that equation (7) becomes the same as equation (6). It can be seen that this latter condition obtains under conditions of high agitation, and this fact is exploited in the present work to determine the reaction rate constant, K_R , for the growth of $MgSO_4 \cdot 7H_2O$, although at lower rates of agitation diffusion was increasingly controlling.

The ratio of the growth rates of different faces of a crystal has proved to be of interest in the case of $MgSO_4 \cdot 7H_2O$. When diffusion is partially controlling and both rates are first order, equation (7) gives the ratio between the rates of growth of two faces as

$$\frac{dm_1/dt}{dm_2/dt} = \frac{\frac{1}{K_{R_2}} + \frac{1}{K_{D_2}}}{\frac{1}{K_{R_1}} + \frac{1}{K_{D_1}}} \dots\dots\dots (8)$$

When the surface reaction controls, i.e. in highly agitated systems,

$$\frac{dm_1/dt}{dm_2/dt} \longrightarrow \frac{K_{R_1}}{K_{R_2}},$$

and when diffusion controls,

$$\frac{dm_1/dt}{dm_2/dt} \longrightarrow \frac{K_{D_1}}{K_{D_2}} \longrightarrow 1.0$$

Thus the ratio of the growth rates of any two faces should lie between 1.0 and some maximum given by K_{R_1}/K_{R_2} .

The Diffusion Process

When the rate of a crystallization process depends at least in part on a mass transfer process, the method of dimensions can often be of help in calculating this rate. Hixon and Knox¹³ have used this method in correlating data from growth experiments on $MgSO_4 \cdot 7H_2O$. In their experiments solutions of known supersaturation were forced past stationary crystals at known velocities and the overall mass growth rates measured. Mass transfer coefficients were calculated on the basis of first and second order surface reactions and related to the crystal size and solution velocity by the equation

$$\left(\frac{K_p d}{D} \right) = 0.48 \left(\frac{dV\rho}{\mu} \right)^{0.6} \left(\frac{\mu}{M D} \right)^{0.3} \dots\dots (9)$$

It was found that the assumption of a first order reaction gave less scatter than a second order reaction. The corresponding surface reaction rate constant was

$$K_R = 0.0111 \text{ gms MgSO}_4 \cdot 7\text{H}_2\text{O} / \text{sec cm}^2$$

at 30.5°C, and the activation energy was 24,300 cal./gm. mole.

For unagitated systems, McAdams¹⁴ has correlated the heat transfer coefficients from stationary vertical cylinders, to allow for natural convection. Hixon and Knox give the analogous mass transfer correlation, involving a modified Grashof number, as being of the form

$$\left(\frac{K_D d}{D} \right) = B \left\{ \left[\frac{d^3 \rho^2 \pi g (S-1)}{\mu^2} \right] \left[\frac{\mu}{M D} \right] \right\}^{1/4} \dots\dots\dots (10)$$

III - BREEDING

Although the fact that addition of a seed crystal to a supersaturated solution often leads to the production of new crystals is widely recognized, there are few references to the phenomenon in the literature, and it has been little investigated. An early and very specific reference to this type of nucleation is that of Miers¹⁵, (1911):

"I have many times noticed that when the appropriate crystal is introduced into a supersaturated solution, which is not strong enough to crystallize spontaneously, it may cause crystals to grow, not only in actual contact with itself, but at some little distance in its neighbourhood."

McCabe¹ has discussed the formation of nuclei in crystallizers and mentions three methods of formation besides spontaneous nucleation. He differentiates between nuclei formed by attrition,

in which vigorous agitation tears fragments from a seed crystal, and mechanical impact, nuclei forming when crystals collide with each other on the walls of the vessel. However, he states that a more important source of nuclei results from the "inoculating influences of the existing crystals", and that breeding of this type is of practical use in controlling crystallizers.

Only four experimental investigations of breeding in solutions are known, two of them quantitative and two descriptive. The first quantitative study of breeding was reported by Ting and McCabe¹⁶ (1934). By adding small crystals to steadily cooled $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solutions at the saturation temperature and observing the solutions, they were able to define two supersolubility curves, both well within the normal metastable region.

The first curve represented the formation of a few crystals at supercoolings between $0.5 - 1.5^\circ\text{C}$ (for cooling rates of $2.4 - 6.0^\circ\text{C} / \text{hr.}$) The second supersolubility curve corresponded to a great shower of crystals, accompanied by a large heat effect, occurring at from $2.0 - 3.7^\circ\text{C}$ supercooling. Under similar stirring conditions, when no crystals were added no nuclei formed even at much higher supercoolings: this clearly establishes the concept of breeding.

Van Hook¹⁷ has observed breeding (which he calls "false grain") in sucrose solutions at high supersaturations, and concluded that the nuclei produced constituted irregular growths detached by agitation. In his fairly detailed discussion of false graining, he states that the region in which breeding occurs extends from about $1.06 - 1.07$ supersaturation, and that the amount of breeding depends

on the number of seeds present and on the stirring, as well as the supersaturation.

Powers¹⁸ has produced nuclei in nucleus-free supersaturated sucrose solutions by spinning sucrose crystals at varying speeds. The nuclei were grown by cooling and counted. When a crystal was spun, nucleation was produced "virtually in a saturated solution" when the stirring speed was sufficiently high. Perspex models of crystals, when spun at similar rates, produced nucleation only at higher supercoolings. To explain why the presence of a crystal caused nucleation at lower supersaturations, Powers suggested that nuclei were shed from the crystal.

Quite recently, Heubel and Devrainne¹⁹ have investigated breeding in aqueous KNO_3 solutions. Adding small numbers of crystals to solutions stirred at 920 rpm, and observing the solutions (as well as plotting the relation between the surface area and mass of crystals in the solutions) they obtained results very similar to those of Ting and McCabe.

A number of new crystals were formed on inoculating the solutions, and these appeared to grow to some critical size. When this size was reached, large numbers of further crystals appeared and, moreover, there was a sharp change in the rate of crystallization of the slurry. Tables 1 and 2 summarize some of their data and give an idea of the numbers of crystals involved. About 60 grams of solution was used in each case. N_1 and N_2 are the numbers of new crystals observed to form in the initial and second nucleations respectively.

Table 1¹⁹ - Effect of a Single Crystal - (KNO_3)

Supercooling, $^{\circ}\text{C}$	N_1	N_2
0.19	220	820
0.30	160	-
0.37	210	3000
0.46	290	5-6000

Table 2 - Supercooling of 0.19°C (KNO_3)

No. of Seed Crystals Added	N_1	N_2
1	220	820
2	440	1280
4	780	920
8	1300	860

Before discussing the results of Ting and McCabe, Powers, and Heubel and Devrainne in more detail the results of the present studies will be presented.

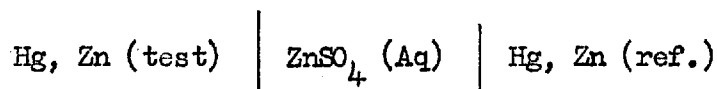
Chapter 2

ZINC - MERCURY AMALGAMS

Benjamin and Strickland-Constable³ have studied the effect of adding small crystals to supersaturated zinc amalgams at less than 1°C supercooling (which was thought to be well within the metastable region) and found that an immensely larger crop of new crystals was produced. They concluded that this was due to breeding. Very accurate control of conditions is necessary in this type of experiment, and the present work was begun with a view to repeating the earlier work under more rigorous conditions, in order to establish the existence (or otherwise) of breeding on a firmer basis.

Zinc amalgams have a fairly convenient solubility of 2 - 4 wt.% in the range 20 - 60°C, and three solid solutions are known.²⁰ In order to avoid the complications of phase change, the experiments were carried out in the region 20 - 43°C, where β -zinc (43 - 53 wt.% zinc) is stable. Good agreement was found with the solubilities as determined by Benjamin and by Cohen and Inouye,²¹ however, due to oxidation over periods of time, the concentrations of amalgams sometimes changed and it was found preferable to determine the concentration of an amalgam by measuring its saturation temperature rather than attempt to make up the amalgams to specified concentrations.

The behaviour of the amalgam under test was followed continuously using the concentration cell technique originated by Benjamin:



When the concentration of zinc in the reference electrode is maintained constant, the emf of the cell is an instantaneous measure of the concentration of the test amalgam:

$$E = \frac{RT}{2F} \log \frac{C_t}{C_r} \dots\dots\dots (11)$$

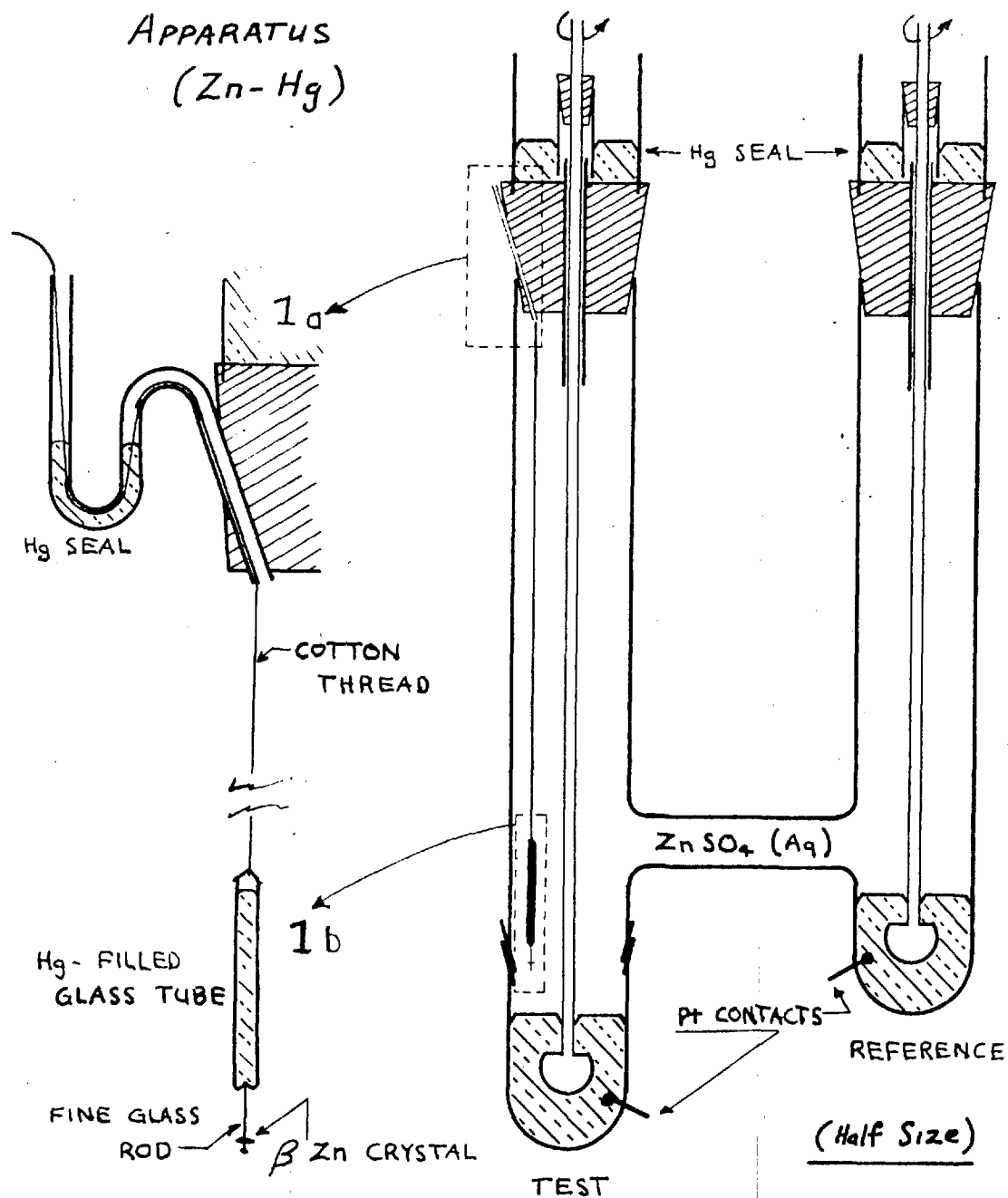
I - APPARATUS & METHODS

The cell used in most of the present experiments is illustrated in Fig 1. It consisted of two glass tubes of about $\frac{3}{4}$ in. diameter and 8 in. length, joined by a short length of smaller tubing. The bottom of one leg of the cell was fitted with a ground glass cone and socket joint to facilitate removal of the test amalgam, and both electrodes were provided with glass stirrers independently driven through mercury seals.

Electrical contact for the emf measurements was made using Platinum wires sealed into each electrode, the wires extending $\frac{1}{16}$ in. into the amalgams. The electrolyte was approximately 2M zinc sulphate. This cell was immersed in a water bath, the temperature of which was controlled within $\pm 0.02^\circ\text{C}$ by means of a mercury-toluene switch fitted with a Sunvic proportioning head.

Figure 1

APPARATUS
(Zn-Hg)



A screw-driven piston was used to adjust the volume of mercury in this switch, and by gearing the screw to a clock motor, accurately controlled cooling rates of $\frac{1}{2}$, $\frac{1}{4}$, and $\frac{1}{8}^{\circ}\text{C} / \text{hr.}$ could be maintained over very long periods of time. More rapid cooling rates were manually controlled.

In the earlier experiments the cell was fitted with a third, smaller, unstirred electrode between the two shown in Fig. 1. This held a very dilute amalgam for use as the reference electrode, whereas the larger electrode, instead of being dilute, was saturated with a large excess of solid zinc. With this arrangement, which was the one used by Benjamin, two simultaneous cooling curves were obtained, as in Fig 2a.

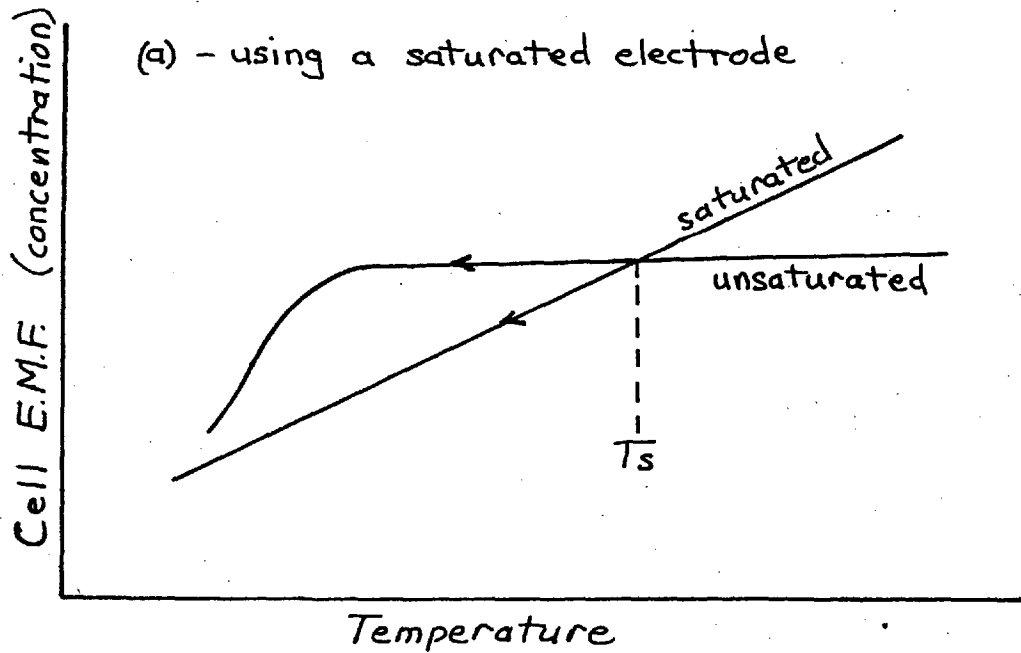
The "saturated" curve represents the change of emf with temperature of a cell consisting of the saturated (with excess zinc) and dilute electrodes, while the "unsaturated" curve is the emf between the same dilute electrode and the initially unsaturated (test) electrode, which begins to crystallize at some temperature below the saturation temperature. It can be seen that, when the emfs of these two cells are the same, i.e., at the intersection of the two curves, the initially unsaturated amalgam is at its saturation temperature (T_s). Thus, by cooling the cell and measuring the emfs it was possible to determine the saturation temperature of a test amalgam.

Unfortunately the above method was not found to work well in practice. The stationary (dilute) electrode was position sensitive, and a slight jar could cause a jump in both emf curves.

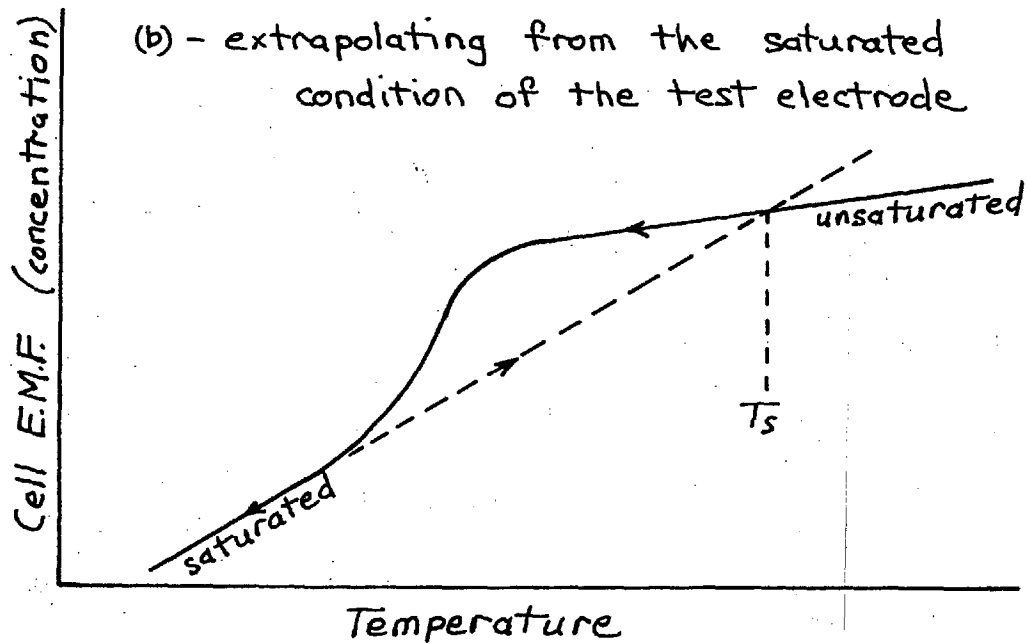
Figure 2

DETERMINATION OF SATURATION TEMPERATURE

(a) - using a saturated electrode



(b) - extrapolating from the saturated condition of the test electrode



Furthermore, the effects of stirring on the emfs of the two stirred electrodes were not always the same. This led to errors in the determination of T_s , as illustrated in Fig. 3, where the results of run No. 52 are plotted. It can be seen that, when crystallization had occurred in the unsaturated amalgam, the emfs of the two saturated amalgams, measured against the same dilute electrode, were not the same. The true saturation temperature of the amalgam was thus considerably higher than that indicated by the intersection of the measured cooling curves.

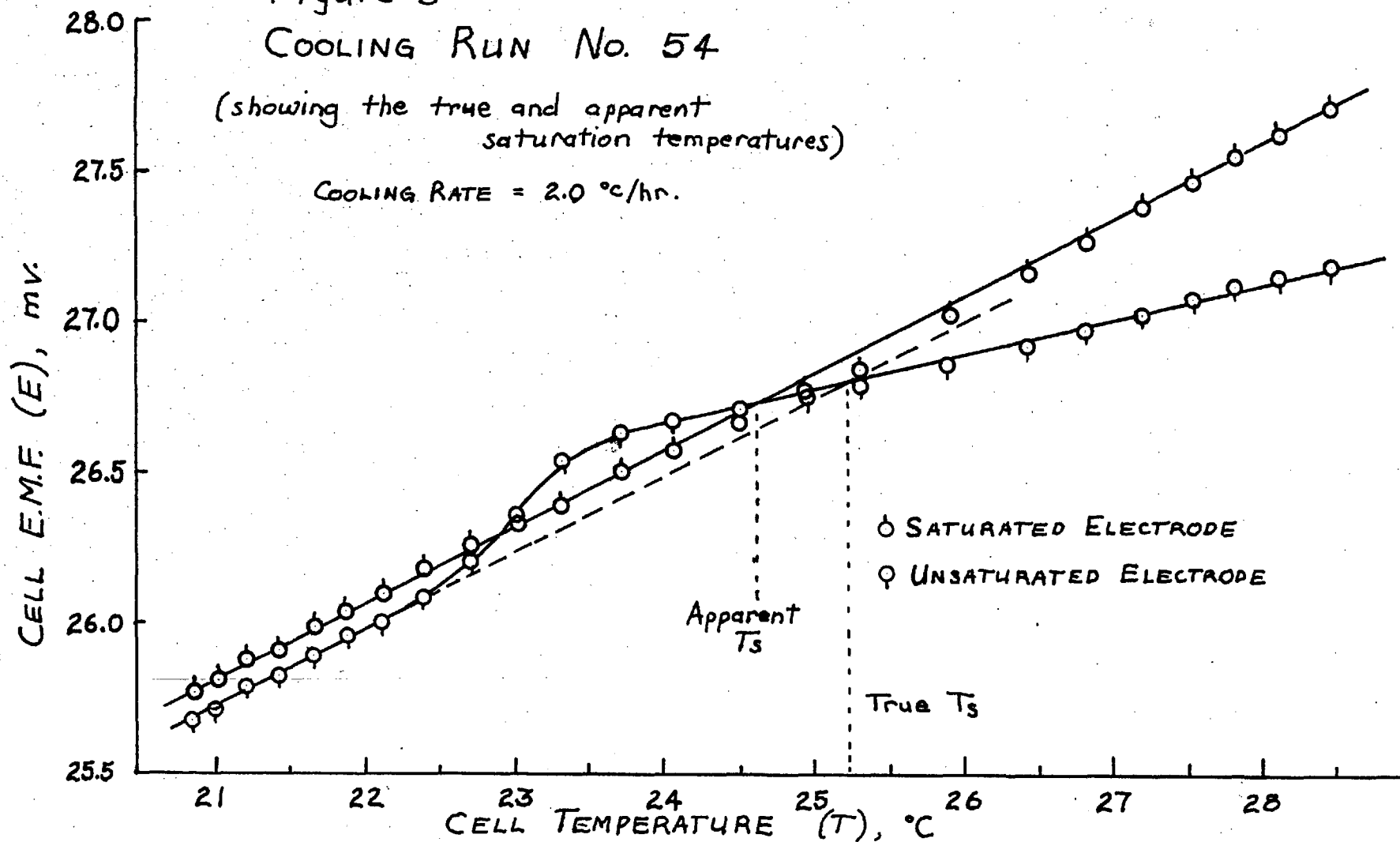
For this reason the method of determination of the saturation temperatures was that shown in Fig. 2b, where only the emf difference between the test and a dilute reference electrode was measured. The saturation temperature was obtained by extrapolating back the saturated portion of this single cooling curve to intersect the initial, unsaturated, portion. In fact, most of the experiments were conducted in the two-electrode cell of Fig. 1, the concentrations of the dilute (ref.) amalgam and the test amalgam being only slightly different so that the activity coefficients γ_t and γ_r were roughly comparable (eqn. 11). Both electrodes were normally stirred.

In setting up the cell, the reference electrode was loaded with about 80 grams of 4 wt. % zinc in mercury. The test electrode was loaded with 60 - 80 grams fresh triply-distilled mercury, and the cell was filled with hot electrolyte solution. To eliminate any oxygen present, the cell was left for at least

Figure 3
COOLING RUN No. 54

(showing the true and apparent
saturation temperatures)

COOLING RATE = 2.0 °C/hr.



12 hours with stirred electrodes, the oxygen being removed by chemical combination with the zinc at the reference electrode. Zinc was transferred electrolytically from the reference to the test electrode at about 50 m.a. current, in order to make up the test amalgam. Thus the absence of impurities in the test amalgam was ensured, although studies indicated no difference in behaviour when clean massive zinc was dissolved in clean mercury. The cell was always pre-heated $10-20^{\circ}\text{C}$ above T_s before beginning a run.

Normally the cell behaved erratically for one or two days, after which smooth curves of emf against temperature could be obtained on cooling the cell. Most of the measurements were made on stirred amalgams and even in the case of stirred cells emf measurements were made without interrupting the stirring (which was 300 - 350 rpm in all cases). This was different from the procedure adopted by Benjamin - a discussion of the effect of interrupting the stirring can be found in Appendix I. Cooling curves were used as previously explained to find the saturation temperature of the test amalgam, and when two or more consecutive runs gave the same T_s , an inoculation run was carried out.

In order to study the effects of inoculation, small crystals were suspended in the amalgams using the plumb-bob arrangement indicated in Figs. 1a and 1b. These inoculating crystals, β -zinc crystals from previous runs, were impaled on a fine glass rod attached to a weighted glass tube, and the device suspended above

the amalgam on a cotton thread. When the desired supercooling had been attained, the bob was lowered until the crystal was submerged.

After inoculation, when the cell emf had been observed to decrease, the amalgam was cooled to room temperature so that the crystals present would grow to more convenient sizes, the cooling being slow enough to ensure that spontaneous nucleation did not occur during cooling. The crystals were separated from the amalgam by centrifuging, the mercury passing through a No. 3 sintered glass disc, and the dry crystals were sorted into various size ranges by hand, and counted.

II - NUCLEATION IN ZINC AMALGAMS

The experimental method required that many cooling runs be carried out in order to determine the saturation temperature of the test amalgams with certainty. In the course of these runs it was noticed that, as might be expected, the supercooling at which nucleation apparently occurred increased with cooling rate. The cooling runs are summarized in Table 6 (Appendix I). This table reports the maximum supercoolings measured before a decrease in the cell emf was noticed:

$$\Delta T = T_s - T_n$$

where T_n is the temperature at which nucleation was first observed. These supercoolings have also been converted into

the corresponding maximum supersaturations:

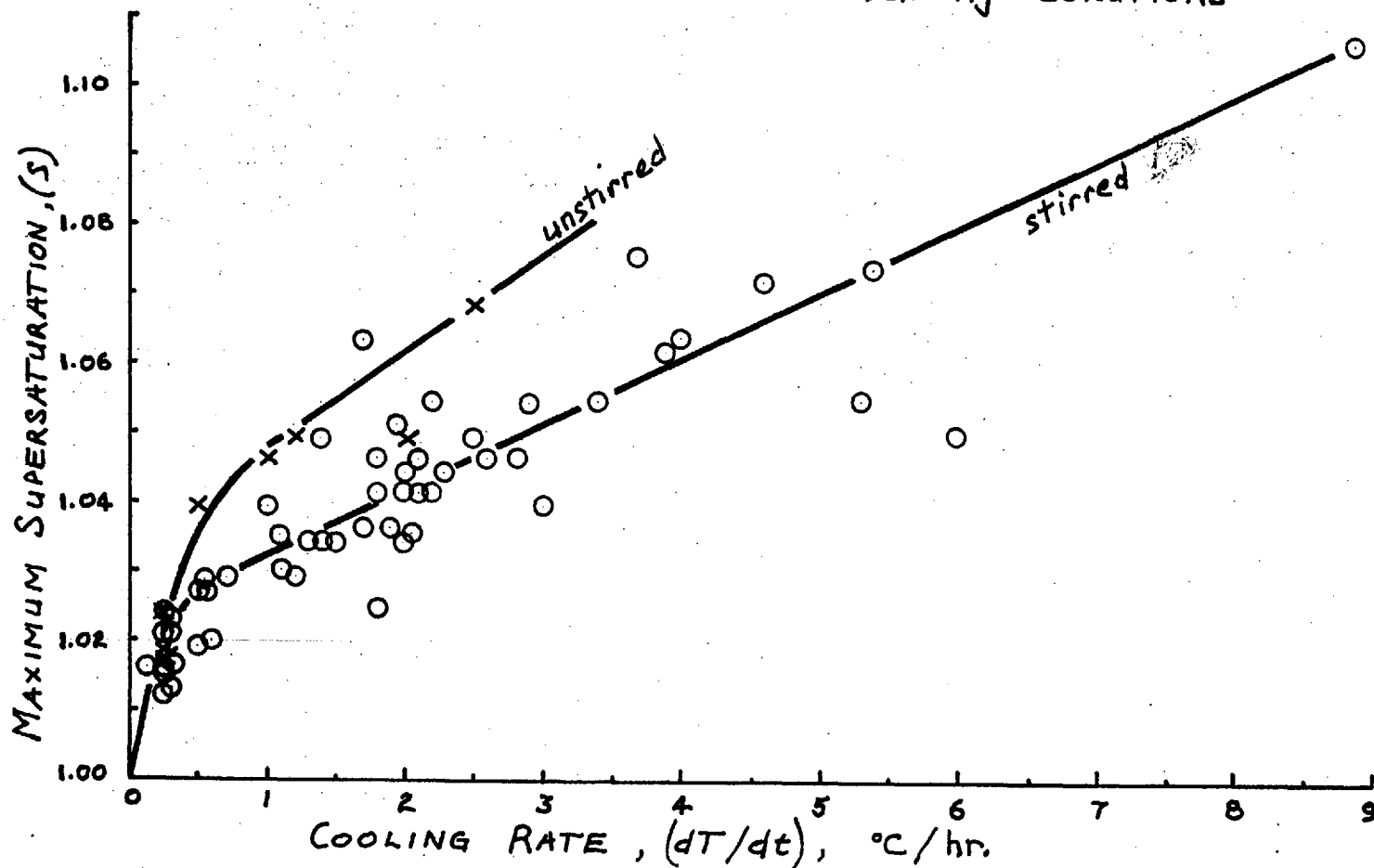
$$S = \frac{\text{mass fraction Zn in solution, temp. } T}{\text{mass fraction Zn in saturated solution, temp. } T}$$

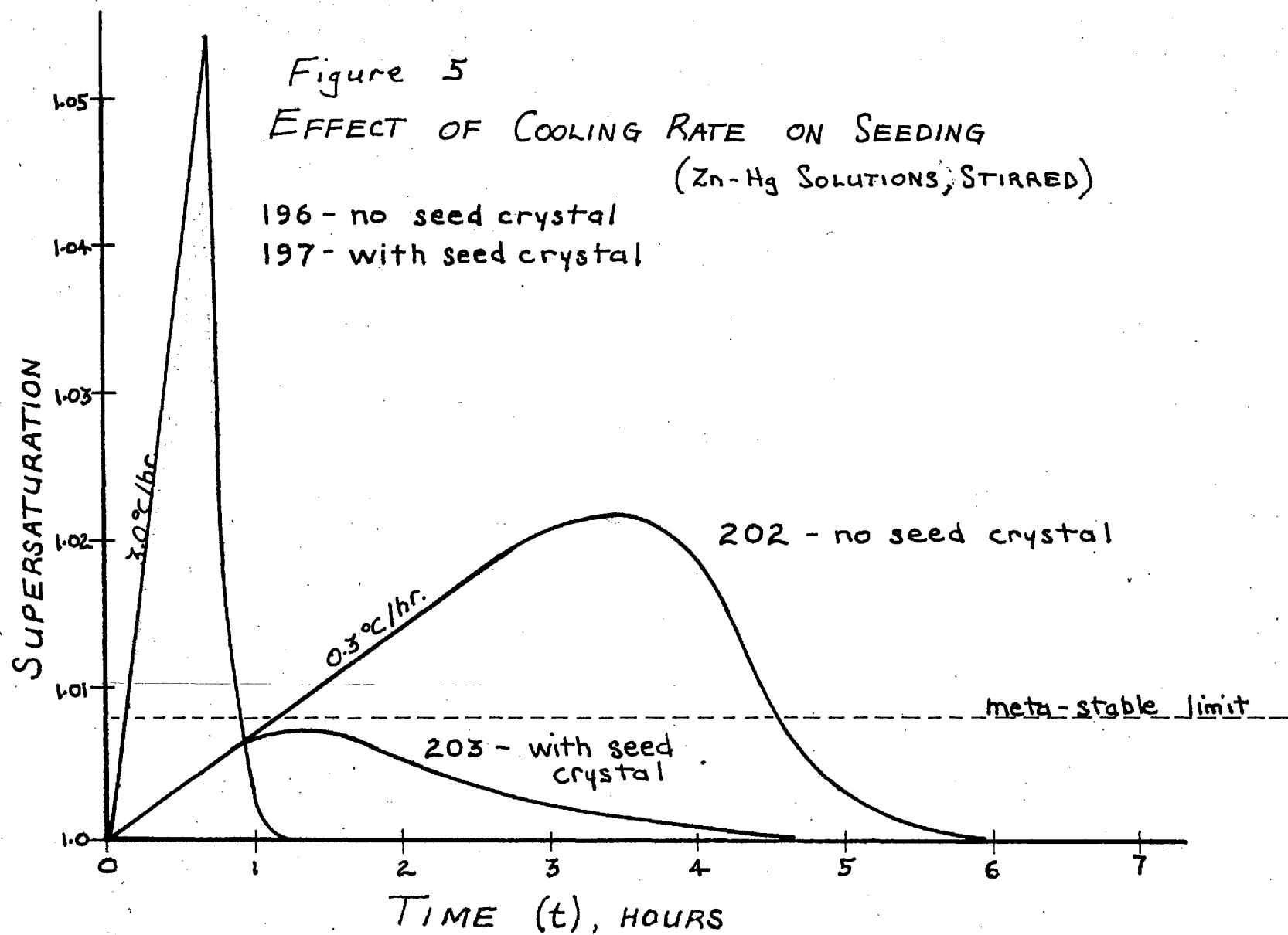
The rates at which the cell was cooled are also reported.

The data of table 6 are shown graphically in Fig. 4, for stirred and unstirred solutions. This figure indicates that, at high cooling rates much greater supersaturations were attained in unstirred cells than in stirred cells, but at cooling rates below $\frac{1}{2}^{\circ}\text{C}/\text{hour}$ this effect of stirring was not evident. The figure also suggests that at cooling rates above $\frac{1}{2}^{\circ}\text{C}/\text{hour}$, for both stirred and unstirred amalgams, the rate of separation of solute onto existing crystals was much less than that due to the formation of new crystals; thus at high cooling rates the reduction of the supersaturation proceeds entirely by the formation of new nuclei.

In order to remove a marginally detectable supercooling of 0.1°C by nucleation alone, for a typical case ($T_s = 27^{\circ}\text{C}$), would require the removal by nucleation of about 30×10^{19} zinc molecules/cc., corresponding to about 10^{18} nuclei (if a nucleus is taken to contain 300 zinc molecules). Nucleation rates capable of producing such numbers of nuclei in a reasonable time will obviously only occur well within the labile region. Thus although nucleation occurs at lower supercoolings than those suggested by Fig. 4, it cannot be detected until the rate of nucleation is very high.

Figure 4
SPONTANEOUS NUCLEATION OF Zn-Hg SOLUTIONS





The effect of cooling rate is shown more clearly in Fig. 5. At a rate of 3.0°C/hr. (runs 196, 197), the addition of a single crystal at the saturation temperature caused no measurable reduction in the maximum supersaturation attained. Thus the rate of crystallization onto the seed was insufficient to remove a significant proportion of the steadily rising supersaturation. Spontaneous nucleation occurred at the same supersaturation in both cases, i.e. with and without a crystal being present, and the supercooling was reduced by a combination of nucleation and crystallization on the greatly increased surface area.

At the lower cooling rate of 0.3°C/hr. the addition of a seed crystal at the saturation temperature was followed by crystallization at a rate which was just sufficient to prevent the metastable limit being reached.

Whereas in run 197 the seed crystal grew into a disc about 1.5 m.m. in diameter and 1 m.m. thick (0.0625 g.), that in run 203 grew into a truncated sphere 3.3 m.m. in diameter and 2.4 m.m. high (the truncation was due to the top of the crystal reaching the liquid surface,) weighing 0.1985 g. From the original size of the seed crystal, it is estimated that the growth rate of β -zinc at 26.5°C and 1.007 supersaturation is about 6×10^{-4} grams zinc/cm²/sec (run 203). Rates of this order would not permit a detectable amount of growth on the seed in run 197: it is estimated that the maximum supersaturation which could have been removed by crystal growth alone in this run, was equivalent to less than 0.05°C supercooling.

Thus the cooling runs indicate that the metastable limit for zinc-mercury is considerably less than $\Delta T = 1.0^{\circ}\text{C}$. They also show that, where it is desired to grow nuclei to convenient sizes, as in a study of breeding, the cooling rate must be less than about 0.3°C/hr . to ensure that the metastable limit is not reached. Since Benjamin and Strickland-Constable did not attempt to keep their cooling rates below this value, it is possible that significant amounts of spontaneous nucleation may have occurred in their work. This would explain why, in their work, the crystal yields following inoculation were substantially the same as those following spontaneous nucleation.

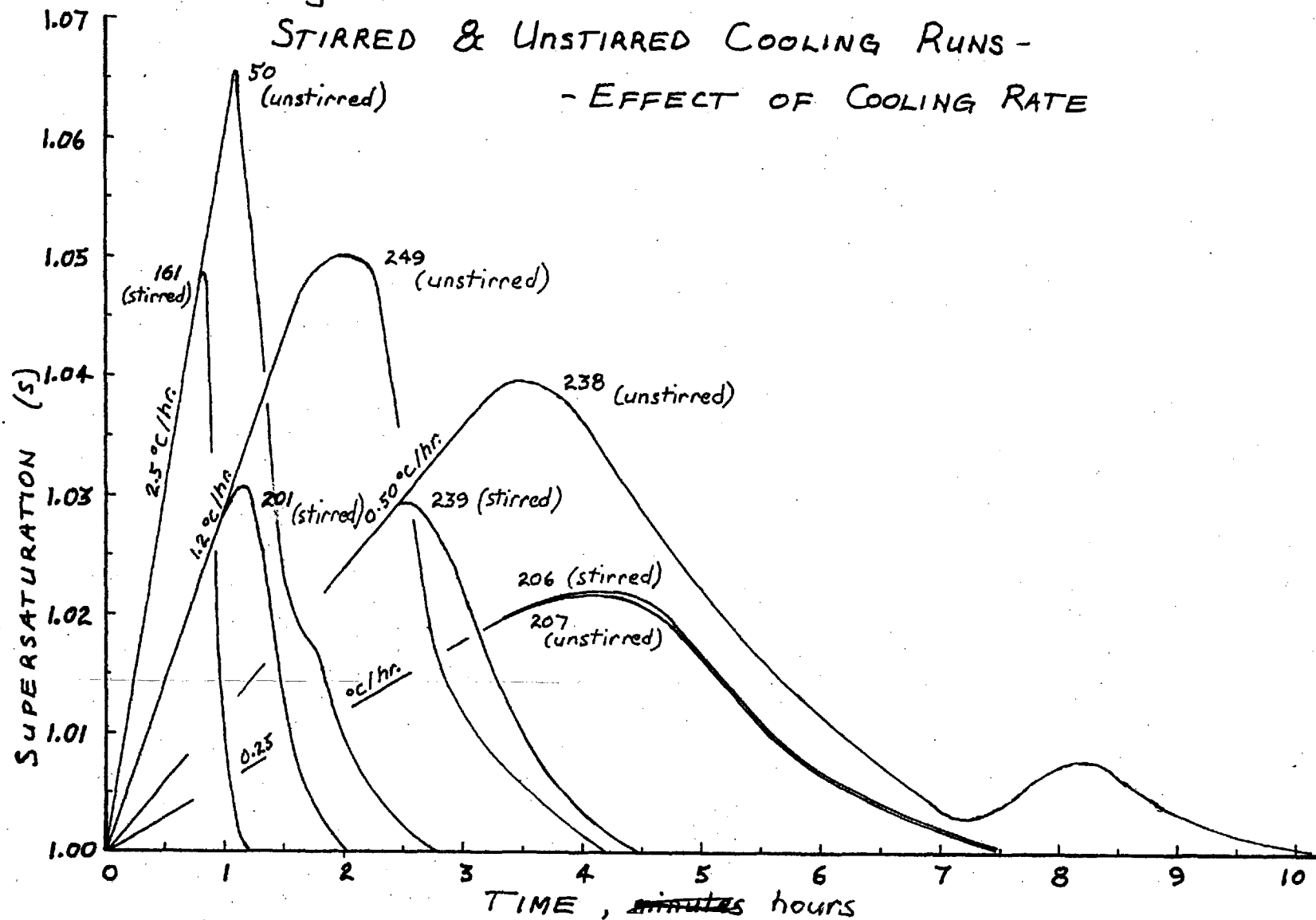
For unstirred solutions, the precautions against spontaneous nucleation are even more important. The higher supercoolings obtainable on cooling unstirred amalgams have been noted in discussing Fig. 4, and are shown in more detail in Fig. 6, which compares stirred and unstirred runs for a range of cooling rates. At cooling rates as low as 0.25°C/hr , it is apparent from the coincidence of the curves (runs 206, 207) that the effect of stirring is less important. (Graph 4 also shows that stirred and unstirred runs are indistinguishable below this rate.)

At the higher cooling rates, the peaks of the stirred curves are much sharper than those of the unstirred ones, since the nucleation rates (and probably the growth rates) are much greater in the stirred amalgams, in spite of the lower supersaturations. Cross comparing runs 161 and 249 indicates that stirring improves

Figure 6

STIRRED & UNSTIRRED COOLING RUNS -

- EFFECT OF COOLING RATE

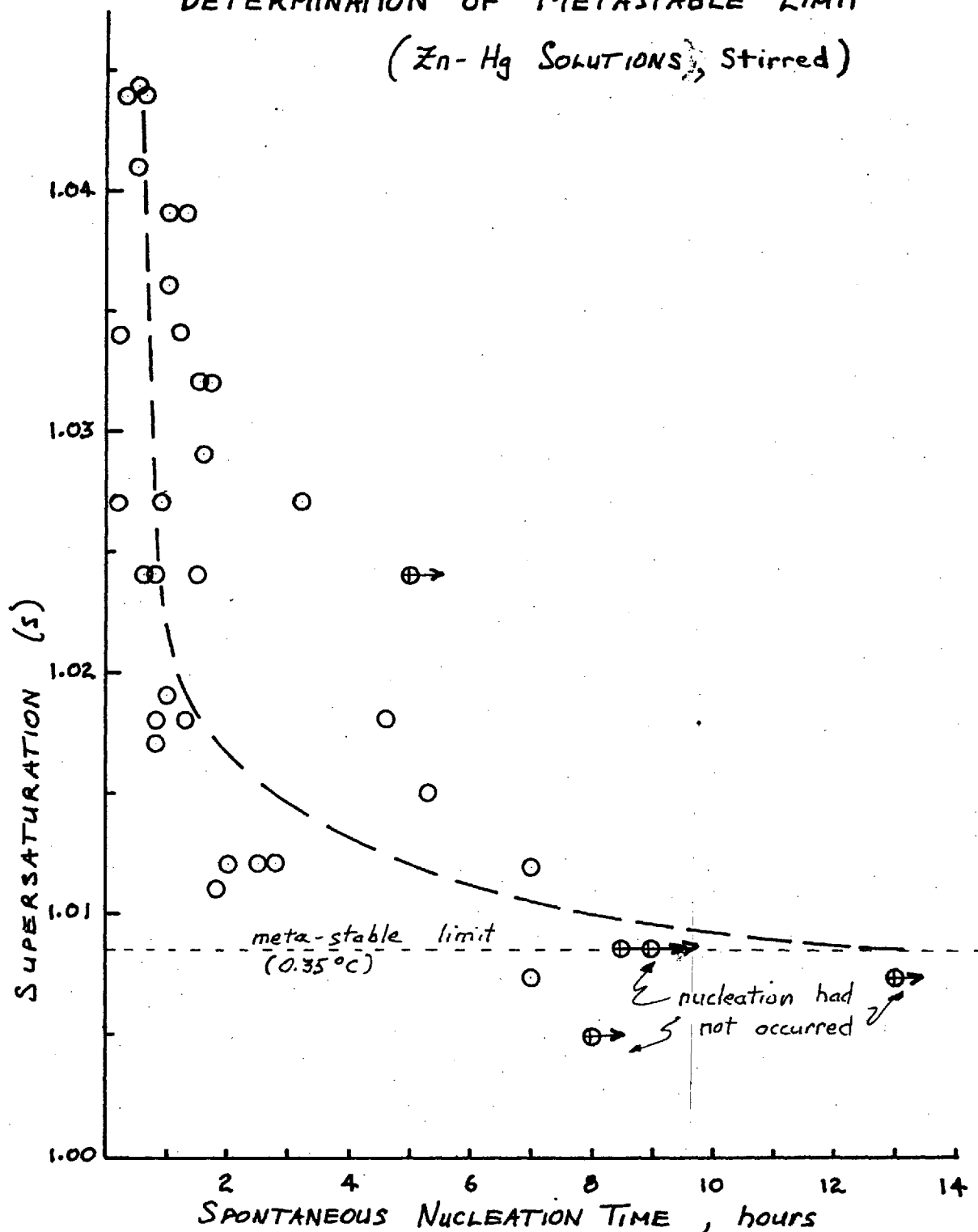


the nucleation rate by a factor of five.

To determine the maximum practical meta-stable limit for the stirred zinc amalgams, a number of runs were carried out in which an amalgam was cooled to a known constant supersaturation and held until crystallization occurred. The time in hours between the solution being cooled and the first crystallization being detected, is reported in table 7 for various supercoolings and saturation temperatures. These results are also shown graphically in Fig. 7, runs where nucleation did not occur being marked with an arrow. From this graph a practical value of the metastable limit can be seen to be about $S = 1.0085$, or 0.35°C supercooling. In only one case was nucleation detected below this value, and that after 7 hours. The high degree of variability in these results is attributable to differences in temperature, stirring, and possibly to inherent differences between the various solutions.

The constant temperature runs in Table 7 have also been used to estimate the interfacial energy in Holloman and Turnbull's equation (3) and thus to estimate the true nucleation rate (calculations in Appendix I). The metastable limit indicated, 0.34°C , agrees remarkably well with the above estimate. Although the experiments of Benjamin and Strickland-Constable indicated a metastable limit of about 2°C , the value of σ obtained by them was only about 10% different from that obtained in the present work. It is, therefore, possible that the true metastable limit was much lower than they thought. As is shown in Appendix I,

Figure 7
DETERMINATION OF METASTABLE LIMIT
(Zn-Hg SOLUTIONS), Stirred)



their results appear to be consistent with homogeneous nucleation above a metastable limit of about 0.35°C .

If this is so, ~~it~~ has important repercussions with regard to their discussion of breeding. Breeding was postulated by them to explain why repeated crystallizations did not appear to remove the heterogeneous particles on which nucleation apparently occurred, as well as to explain the very large numbers of crystals obtained on seeding solutions at the "slight" supercoolings between 0.5 and 1.0°C . It now seems likely that these effects were the result of exceeding the metastable limit, and that Benjamin and Strickland-Constable may not have observed breeding.

III - BREEDING IN ZINC AMALGAMS

Analysis of the present series of inoculation runs, carried out under carefully controlled conditions, has shown that breeding does occur in zinc-mercury solutions. Table 9 is a summary of the ten inoculation runs for which a complete set of data was available. (A loose copy of this table may be found in the folder at the end of the thesis.) In most of these runs the cell was held at a temperature which resulted in a small constant supersaturation, and then a β -zinc crystal was introduced as previously described (section I). After the cell emf had been observed to decrease, the cell was cooled at the rate indicated until room temperature was reached.

The inoculating crystals, 1 - 2 m.m. in diameter, and weighing

from 0.001 - 0.014 grams, were suspended on the plumb-bob arrangement shown in Fig. 1b in all cases except run 155, in which the crystal was simply dropped free into the amalgam; they were left in the amalgam throughout the cooling period except in run 186, in which the seed was withdrawn after 12 minutes. The stirred amalgams were stirred at 300 - 350 rpm without interruption from beginning to end with the exception of run 247, where the stirrer was stopped after about 3 hours.

In no case was the supersaturation allowed to exceed the metastable limit during the cooling period, except for run 197, which has previously been discussed (p. 33). Any supercooling during the cooling period was usually undetectable, i.e. less than 0.1°C .

Four of the runs, marked "continuously cooled" in the table, were not inoculated at a constant supercooling as described above. Instead, the seed crystal was added at or a little above T_S , and the amalgam was cooled continuously at the specified rate to room temperature. Thus these runs may be considered as representing inoculation at 0°C supercooling. However, slight supercoolings were obtained in these runs. Fig. 5 has shown the maximum supercooling reached in run 203. Smaller values were reached in the other runs, and these were all less than the metastable limit. Again, run 197 is an exception to this, the metastable limit having been greatly exceeded.

The crystals obtained were in most cases thin shiny discs such as Benjamin and Strickland-Constable described, but many thicker

prisms, often with depressed faces, were also produced. These usually constituted the larger crystals reported in Table 9. Crystals from the unstirred amalgams were hexagonal, as were most of the smaller crystals from the stirred amalgams; the larger crystals from stirred amalgams were rounded.

Growth of the inoculating crystal occurred in all cases, the largest of the resultant crystals being best described as porous and apple-shaped. In one run (208, unstirred,) a cluster of individual crystals, of a range of sizes up to 3 m.m. dia., was obtained around the seed crystal. The seed in run 271 (also unstirred) grew a single attached thin hexagonal crystal, about 4.5 m.m. across, with slight v-notches (of about 160°) in each hexagonal side. This crystal grew perpendicular to the plane of the seed itself, the seed forming one of the sides of the hexagon. The gain in weight of the inoculating crystals varied from 50% (run 155) to 5000% (run 216). Such growth is included in the yield figure but does not otherwise appear in table 9.

In order to permit a rough assessment of the reliability of the runs, table 9 includes the weight yield of crystals obtained. This is reported as grams / c.c. $^{\circ}\text{C}$, and was obtained by adjusting the measured yield in each case according to the total weight of amalgam used and the temperature difference ($T_s - T_f$), T_s and T_f being the saturation and final temperatures, respectively. The yields were generally about 30% higher than the theoretical yield of 0.016 g. / c.c. $^{\circ}\text{C}$, due probably to excess mercury on the crystal surfaces. In one case, run 216, T_f was unfortunately below room

temperature and it is possible that some of the growth may have re-dissolved before or during centrifuging.

As has been mentioned, the crystals obtained after centrifuging were graded as to size by hand. The numbers of crystals of the various sizes are reported in Table 9 as the number per c.c. of solution, so that the total numbers obtained were usually four to five times greater than the figures shown.

IV - DISCUSSION OF BREEDING RESULTS

Examination of Table 9 shows that some breeding of crystals has occurred in all cases, including the two unstirred runs, 208 and 271. Many more crystals were formed in the stirred amalgams than in the unstirred ones, and the crystals were generally much smaller. Furthermore, in the stirred amalgams in which a range of crystal sizes was obtained, there were more smaller crystals than larger ones.

Although the large number of crystals of less than 0.5 m.m. diameter were the outstanding characteristic of the stirred amalgams, they were not the result of attrition alone, since the total amount of stirring did not affect their numbers. For example, 1500 crystals per c.c. were obtained in each of runs 243 and 247, which were stirred for 23 and 3 hours respectively, the other variables being the same.

On the other hand, the contribution of attrition towards the numbers of crystals formed would be greatest at high supercoolings:

table 8 shows the critical nucleus sizes (n^*) for various supercoolings, and indicates that the size of crystal particle which would grow below 0.1°C supercooling (the condition during the cooling portion of a run) is about 40 times larger than at the metastable limit. Thus, after the initial supersaturation was removed, the chances of nuclei forming by attrition were very much decreased.

Fig. 8 indicates that attrition through impact of the seed with the stirrer or cell walls is not important even at the highest supercoolings. It shows that the rate of removal of the initial supersaturation was greater when the crystal was fixed (186), as normally, than when it was free to collide with the walls and stirrer (155). This graph also indicates that growth is more rapid when the relative velocity between crystal and solution is greatest - i.e., diffusion is a factor.

That the crystals less than 0.5 mm across represent breeding at the time of inoculation is shown by Fig. 9. The linear relation indicated between the initial supercooling and the number of crystals formed could only occur if the formation of the crystals took place when the initial supercooling prevailed. Thus these very small crystals could be the result of attrition following the detachment of irregular growths from the seed. If the irregular growths do not remove a significant proportion of the initial supercooling, a relation such as that in Fig. 9 would be expected.

In view of the later observations on KBr and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, it is believed that these small crystals might also be the result

Figure 8
INOCULATION OF Zn-Hg SOLUTIONS

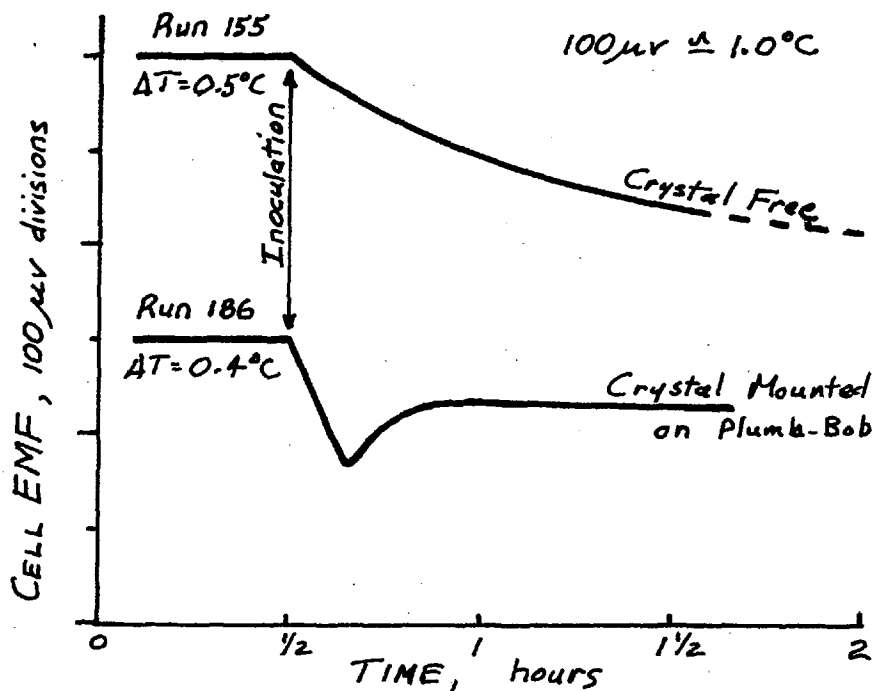
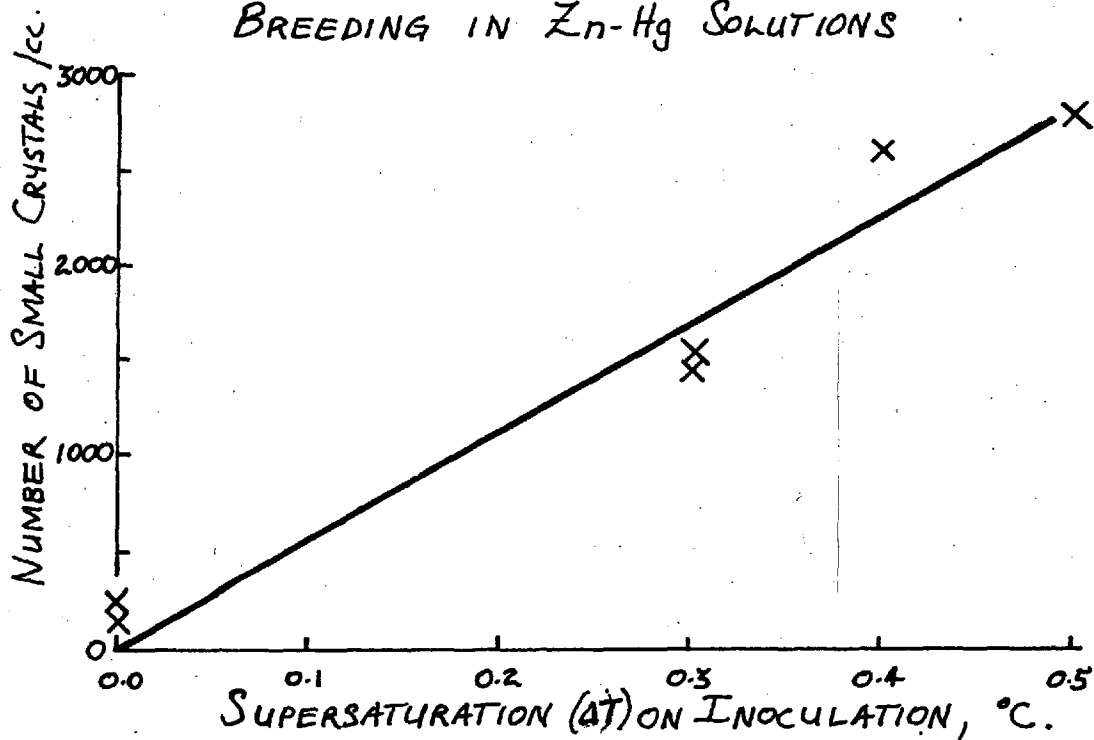


Figure 9
BREEDING IN Zn-Hg SOLUTIONS



of "splintering" - the detachment of irregular growths from the seed producing great numbers of potential nuclei in the form of small fragments. It is, however, impossible to state which of these two mechanisms is the more likely.

It will be noted that both the attrition and the splintering mechanisms make it necessary to hypothesize the growth and detachment of irregular crystal forms; the direct observation of attached growths in the unstirred runs supports this hypothesis. It is further observed that, although the numbers of free crystals in the unstirred runs, 208 and 271 were 10 and 30 respectively, if the number of attached growths in run 208 was considered, the total number of crystals formed was about the same in each case.

The fact that such a large proportion of the crystals became detached in even unstirred runs is indicative of the weakness of their attachment. However, some of the nuclei were undoubtedly fairly strongly attached, and it is thought that some of the larger crystals obtained in the stirred runs may have been due to some nuclei remaining attached to the seed for significantly longer times. During the time of attachment, their velocity relative to the solution would be greater than for similar free nuclei, and, as Fig. 8 suggests, they would grow more quickly.

These hypotheses explain the two major features of the breeding results: the variations in size among new crystals from stirred amalgams, and the relation between the number of smallest crystals and the initial supercooling. The cause of the growths on the seed, which are apparently responsible for both these phenomena, is not

known, but in view of the method of mounting the seeds (which involved piercing the crystal completely,) irregular growth from flaws in the seed is a likelihood.

Chapter 3

AQUEOUS KBr SOLUTIONS

Because the processes occurring in the zinc amalgams could not be observed directly an investigation was begun on aqueous systems. KBr was selected because of its relatively steep solubility curve, which permitted the use of supersaturations of the same order as with zinc-mercury but at more convenient supercoolings. Thus, a supersaturation of 1.0085, corresponding to 0.35°C ΔT for Zn - Hg, occurs at $\Delta T \approx 2.0^{\circ}\text{C}$ for aqueous KBr. It was also known²² that alkali halide solutions do in fact tend to produce showers of crystals when seeded.

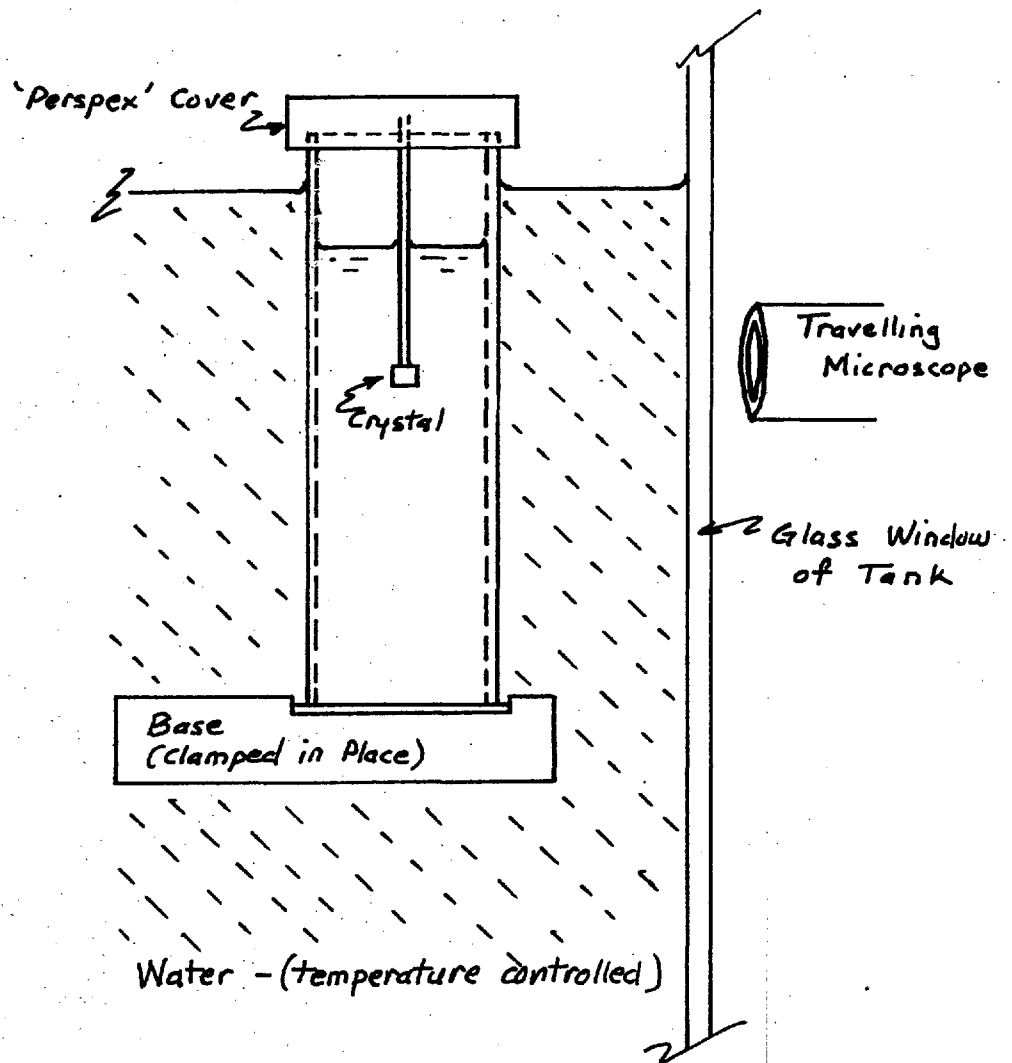
The solubility data for KBr from different sources^{23, 24} were in considerable disagreement and a new determination (Appendix II) has shown that the most recent values²³ are the best.

I - APPARATUS & METHOD

Fig. 10 is a full size sketch of the apparatus used to investigate the effects of seeding supersaturated aqueous solutions. A glass cell, made up from microscope slides bonded by Araldite adhesive, and containing the solution, was immersed in a temperature controlled water bath to a depth of about $2\frac{1}{2}$ in. The cell was located about 1 in. from the glass front of the bath container so that the seed crystal could be viewed through a travelling

Figure 10

SKETCH OF CELL IN PLACE



microscope with a 2 in. objective, giving both a high degree of magnification and good circulation of water on all sides of the cell.

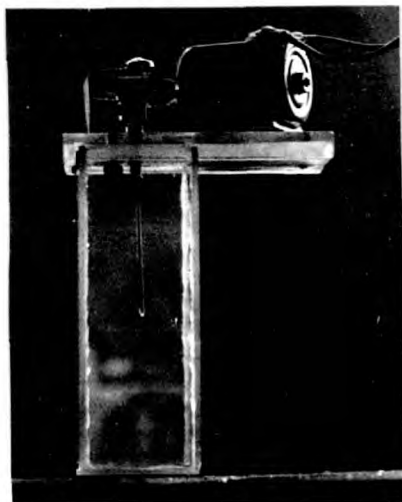
The seed crystals were mounted centrally on fine bore stainless steel tubes using Durofix adhesive, and the tubes were in turn centrally mounted on Perspex covers made to fit the cells. When in position in the cell, the seed crystals were immersed to a depth of at least $\frac{1}{2}$ in., and were about $1\frac{1}{2}$ in. from the cell bottom. Since it was desired in many cases to rotate the crystals in the solutions, three special cell covers were made on which were mounted small 1.5 v. D.C. motors, with geared drives. These are shown in Fig. 11. The motors, whose normal (unloaded) speeds were 6-7000 rpm, were geared so as to make possible the use of any speed from 40 to 6000 rpm.

In preparing for an experiment quantities of filtered solution were made up (using Analar KBr and distilled water) and the saturation temperatures determined by titration against a standardized solution of AgNO_3 . A sample of the solution was placed in the cell, weighed, and then immersed in boiling water for up to 10 min. in order to dissolve any nuclei present. Bias caused by possible evaporation during this procedure was estimated to be less than a maximum of 0.2°C . The solution was stirred and the cell was immediately transferred to the controlled temperature bath, at 32.5°C . At least 10 min. were allowed for the cell to cool to the pre-set bath temperature, after which the seed crystal was introduced into the solution.

Figure 11

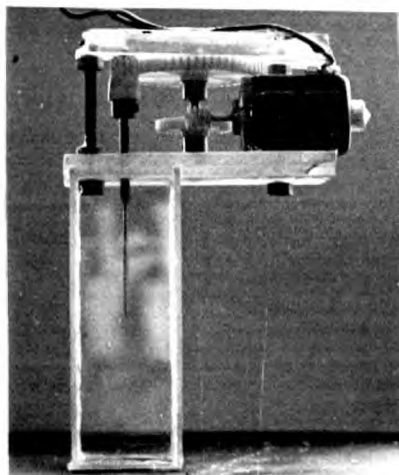
CRYSTAL ROTATION APPARATUS

40-250 rpm



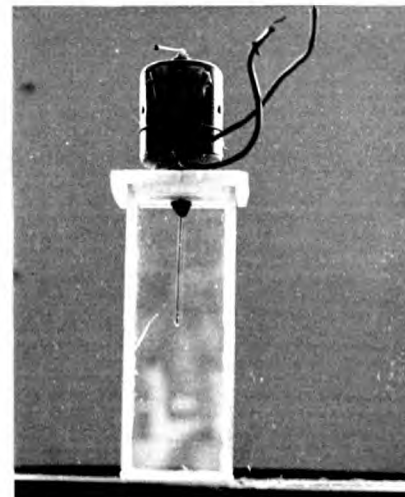
$\times \frac{1}{2}$

150-1200 rpm



$\times \frac{1}{2}$

1000-6000 rpm



$\times \frac{1}{2}$

Using the travelling microscope, the rates of advance of the crystal faces in both the downward and transverse directions were measured where possible. In most of the stirred runs only the downward rates were measured, since otherwise it was necessary to interrupt the stirring. Since the crystal habit is cubic, the downward and transverse growth rates should be the same, but with unstirred and slowly stirred crystals differences in rate were noticed. The growth rates were usually fairly constant over the whole period of the run, but when they were not the initial rate was recorded.

The seed crystals used for inoculation of the KBr solutions were of two types, but no differences were noticed in their effects. In runs 346-51, inclusive, small dendritic crystals up to 1 m.m. across were used. These were produced by dropping a tiny KBr crystal into a still solution at the saturation temperature and then allowing the solution to cool about $2-5^{\circ}\text{C}$, whereupon from two to many hundreds of similar small dendritic crystals appeared, scattered around the original seed. Those which were not in contact with neighbouring crystals were removed and used as seeds.

In the runs subsequent to run 351, the inoculating crystals were extremely smooth surfaced, translucent KBr crystals from $\frac{1}{2}$ to 2 m.m. across. These were produced in the same way as the previous seeds, but the cooling of the solution was much slower, ($1^{\circ}\text{C} / \text{hr.}$ or less) and was continued for over 8°C . A mass of KBr crystals covered the bottom of the flask after this treatment and those on the upper surface of the mass were extremely perfect. Many of

these crystals were elongated and were found to be easily plastically deformable - one such crystal was 10 m.m. long, with a cross-section about $\frac{1}{2} \times 1$ m.m. Such plastic crystals have been described by Amelinckx²⁵ and Gordon²⁶ in the cases of KCl and NaCl. Roughly cubic portions of these perfect crystals were broken off and used as seeds in all runs from 352 onward.

As has been mentioned, most of the runs were carried out at a temperature of 32.5°C, the solution concentrations being varied to vary the supersaturations. In the final series of runs (413a - 418b), however, a single solution saturated at 39.6°C was used, the supersaturation being varied by changing the temperature of the bath. About 300 grams of solution, contained in a 250 m.l. flask, was used for these runs, all the other experimental conditions being the same as in the previous runs. No differences in breeding behaviour were noticed between these runs and the preceding ones.

II - NUCLEATION IN KBr SOLUTIONS

Because of the extremely low metastable limit of the zinc-mercury solutions, the experiments with that system were all carried out in a very small temperature range near the metastable limit, and great care was necessary to ensure that spontaneous nucleation did not occur. In the case of the KBr solutions it was found that spontaneous nucleation did not occur in unstirred or violently stirred solutions up to at least 6°C supercooling, the maximum in these experiments. (See run 360, table 12.)

III - CRYSTAL GROWTH IN KBr SOLUTIONS

The growth rates of KBr crystals, both stirred and unstirred, are reported in table 11. Normally the seeds were grown unstirred for a time, followed by a stirred period. Unstirred rates were measured immediately on immersing the seeds, over the period indicated in the column headed "Immersion Time". The depletion of the solution was calculated from the observed crystal growth, so that the solution concentration when stirring was started was known.

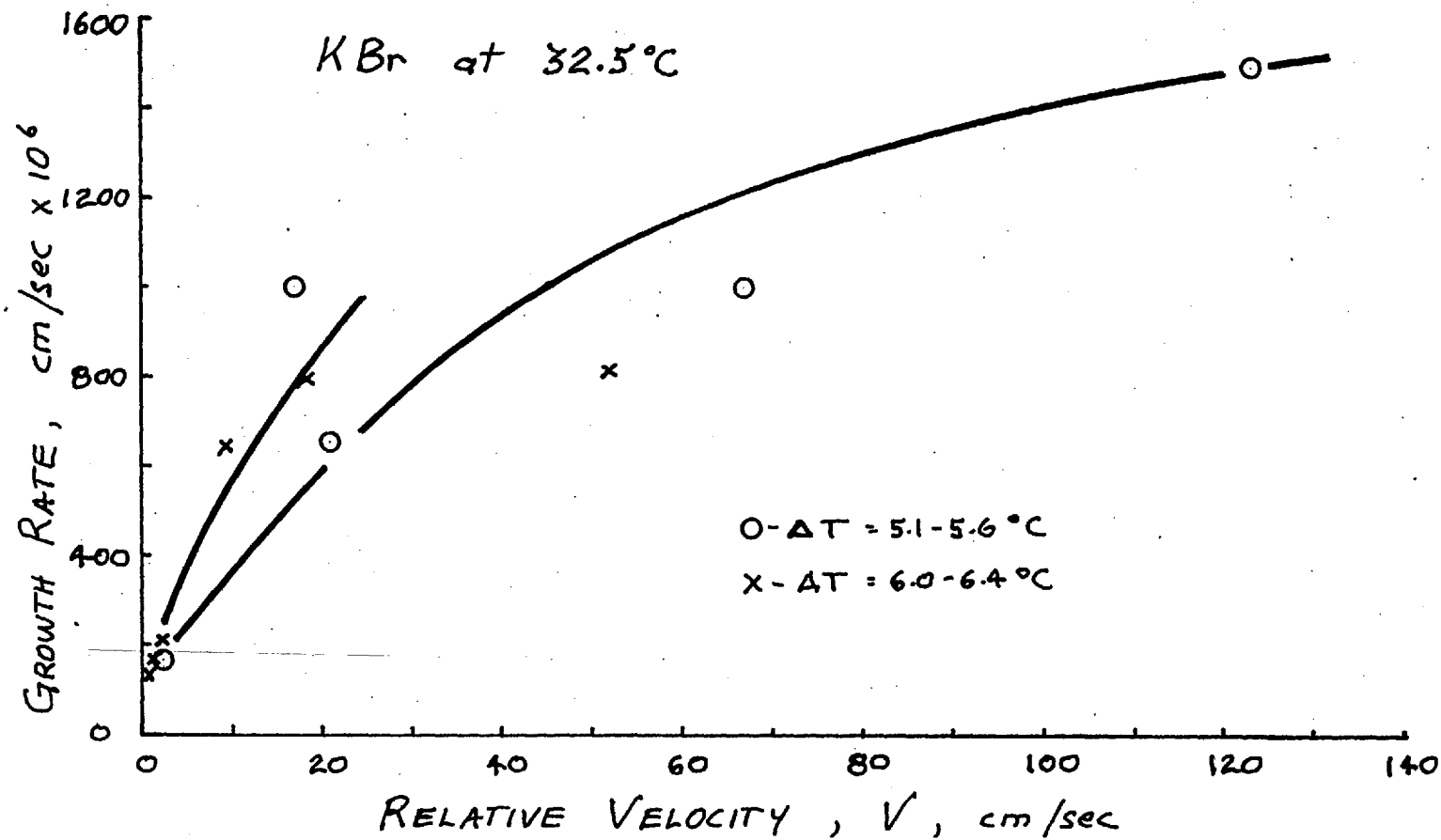
A measure of the effects of stirring is given by the Relative Velocity between the crystal edge and the solution, calculated as

$$V = \sqrt{2} \pi d_s N$$

where d_s is the crystal width when the stirring was begun. The values given in table 11 are initial values only: as the crystals grew the velocity increased. The effects of increasing relative velocity were not normally noticed, the growth rates usually being constant over the stirring period.

Comparison of the stirred and unstirred growth rates in table 11 shows that the rates were greatly increased by even moderate stirring, an indication that the growth rates were partially diffusion controlled. Although it might be expected that the effects of diffusion could be easily eliminated by stirring²², this was not found to be the case, at least for supercoolings above 5°C. Fig. 12 shows the effect of stirring on growth rate for two different supersaturation ranges, with stirring speeds as high as

Figure 12
EFFECT OF STIRRING ON GROWTH RATE



5000 rpm. It can be seen that even at the highest stirring rate, the growth rate is still increasing.

Because of the diffusional effects, the functional relation between growth rate and surface supersaturation could not easily be determined. But if a one to one relation exists, then the observed growth rate can be taken as a useful variable, since it will correspond to a definite surface supersaturation. Thus the stirred growth rates have been reported, where measured, in table 12 as a relative measure of the surface supersaturation, against which the breeding results can be compared.

Growth FORMS

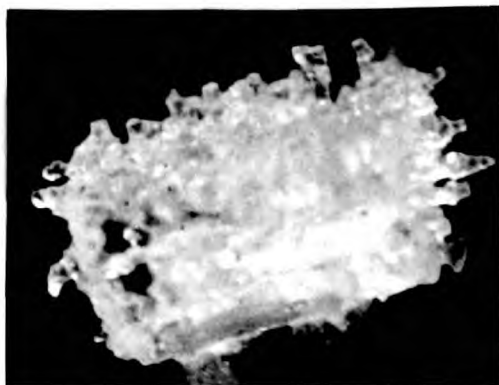
It is of importance to the description of the breeding results which follows to note that the growth of KBr crystals which occurred in all the experiments was imperfect. Thus the crystals were mechanically weak and relatively large crystal particles were often detached by gravitational or centrifugal forces. Two different forms of KBr crystal were obtained and a brief description of each of these follows. Both, however, were imperfect, and no difference was noticeable between the two forms, as regards breeding.

At low supersaturations, below about 4°C , the crystals formed were highly irregular as in Fig. 13a. The surface of the seed was covered with many small projections which grew only approximately normal to the seed faces, and growth proceeded by the further propagation of these projections, which were usually clear, rectangular, and unbranched. When such a crystal was rotated, it

Figure 13KBr GROWTH FORMS

Aggregate

(a)



x 14

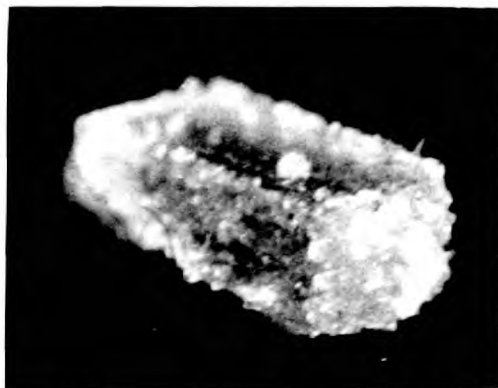
(b)



x 3

Single Crystal

(c)



x 20

(d)



x 3

developed into a rounded aggregate such as that in Fig. 13b, where the surface of the aggregate appeared to show a great many faces and corners in a random arrangement.

At supercoolings above about 4°C , single crystals were produced. In unstirred solutions these were hopper crystals, growth being by the apparent growth of cubes at the crystal corners and edges, as in Fig. 13c. Phillips²⁷ has described such growth as "parallel dendritic" growth. On rotating this type of crystal, the growth became more even, with the face centres no longer being depressed. Thus crystals such as that in Fig. 13d were produced, being definitely cubic in outline, with each face composed of a great many parallel individual faces.

Examination of single samples of each of these types of crystal, using an optical goniometer and X-ray diffraction techniques, has shown that the visual differences do in fact correspond to differences in the crystal structure. The aggregates were seen to be composed of many highly disoriented crystals, and the "cubic" crystals were single crystals with a great many parallel faces. These studies are reported in Appendix II.

IV - BREEDING IN KBr SOLUTIONS

Table 12 (a loose copy can be found in the pocket at the end of the thesis) is a summary of the breeding results in stirred KBr solutions. The stirred growth rates are reported in order to assess the relative surface supersaturations, and the relative velocities

between crystal and solution indicate the effects of stirring. The type of crystal obtained, aggregate (A) or single crystal (s) is also reported, these descriptions referring to the previously discussed crystal forms.

Two types of breeding are reported. The detachment of large crystal chunks on stirring is reported as "True Breeding" and the appearance of a shower of crystals (or of other free crystals) as "Splintering". A description of the overall observations follows.

Initial Breeding Effect

Introduction of the seed crystal into an unstirred supercooled solution at any supercooling was often observed to result in the almost immediate appearance of a few small crystals on the cell bottom. This was attributed to the presence of small crystal particles on the seed crystal - the existence of such particles being indicated by the occasional growth of small crystals from the support rods. Thorough washing of the seeds was difficult because of their high solubility, but such crystal particles were sometimes removed simply by dipping the seed briefly in distilled water before inoculation (these crystals are noted in table 12 as having been added "wet").

When a crystal was removed from the solution, dried, and re-introduced, (Runs 413d, 414c, 416 b & c), similar crystals to those described above quickly appeared. It seems possible that the drying of a crystal results in the production of unattached or loosely attached crystal particles on the surface of a seed - in this

connection it is interesting to note the occasional growth of whiskers from drying seeds (appendix II, p 117).

An explanation of this breeding phenomenon in terms of crystal dust would suggest that it is only of trivial interest. Since the crystals which did appear on the cell bottom were not disturbed by agitation, they could be safely ignored.

True Breeding

In about half the runs in table 12, it can be seen that what has been termed "true breeding" occurred. In fact, this consisted of the detachment of relatively large crystal particles (see Fig. 13a & c) and normally occurred only after stirring was started; it is evident that the mechanical weakness of the imperfect growth forms obtained is an important factor. In two runs (351, 363) this growth was so weak that large crystal pieces were observed to fall from the seed even before stirring was begun.

Splintering

In many of the runs, showers of crystals were observed to form in the region of the seed crystal when stirring was started. In all cases these occurred 10-30 seconds after crystal particles were observed to fall from the seed. Table 12 indicates this coincidence - splintering occurred when true breeding occurred, and did not when true breeding was not noted.

The crystals formed were small (being initially invisible) and were further differentiated from those produced by true breeding

by their great numbers - up to many hundreds . When the seed crystal shattered completely on stirring (runs 355, 367), very large showers were produced, and although the crystals could not be counted, their numbers seemed to be greater at greater supercoolings.

It seems certain that these showers were the result of splintering - small fragments of greater than critical nucleus size being produced when crystal particles were detached from the seed crystal. A very similar phenomenon has been observed by Brewer and Palmer²⁸ when ice crystals fell from the walls of a cloud chamber, producing a secondary copious shower. Their observations are described in more detail in Chapter 5.

Other Observations

In two runs (362, 365) a few crystals were observed in the solution although no irregular growths were seen to fall from the seed. Since in both cases the stirring was very great, it seems possible that very small growths were detached by the stirring, to form new nuclei. This explanation is similar to that offered by Powers (see p. 19) to explain his results with sucrose, and is discussed more thoroughly in Chapter 5.

The effect of attrition through impacts between a crystal and the cell walls was tested in Run 418b. A spinning crystal was lightly touched to the cell walls, no visible particles being detached. After a few seconds, a shower of thousands of tiny crystals appeared, suggesting that when free crystals are allowed

to collide with the walls, attrition would be a very important factor. Attrition also accounted for the fact that, when splintering occurred and the stirring was not immediately stopped, the solution went solid with small crystals and no growth rate measurements could be made.

Besides the observations of breeding of one kind or another, it is of particular importance to note that it seemed to be possible to grow KBr crystals without breeding occurring, as table 12 indicates, and in one run (413c), not even the initial breeding phenomenon was observed. The condition necessary for the elimination of breeding would seem to be the occurrence of strong, compact crystal growth.

Chapter 4

AQUEOUS $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ SOLUTIONS

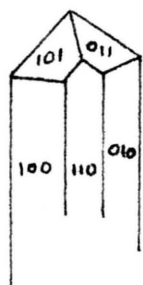
I - APPARATUS AND METHOD

The apparatus used to investigate the breeding phenomenon in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solutions was the same as that used in the case of KBr (see p.47). Only slight modifications of the techniques were necessary.

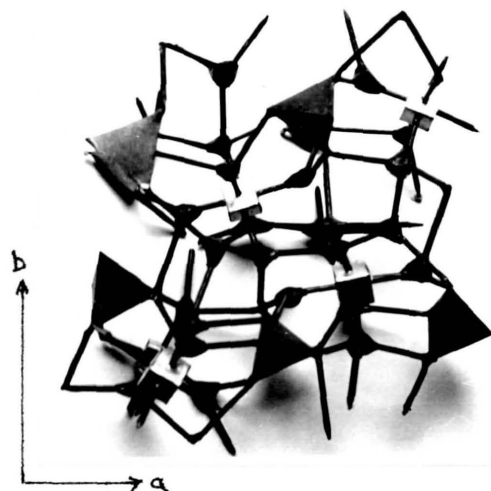
A partial model of the molecular structure of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was constructed, and is shown in Fig. 14, along with a sketch of a typical crystal. The structure is of the $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ type, and the model was based on a structural map of this salt.²⁹ The lattice constants are 11.91, 12.02, and 6.87 Å³⁰. Because the [100] and [010] axes differ by only a small amount in length, these were not differentiated, and they are referred to throughout the thesis as the "a-b" axes or directions. The [001] axis, the long axis of the crystal, is referred to as the "c" axis.

Since the rates of growth in the a-b and c directions differed, it was desirable to measure both rates for both rotated and stationary crystals. This was done most conveniently by growing the crystals vertically, rotation being about the c axis. In the case of rotated crystals, measurement of the rates of advance of the crystal faces necessitated stopping the rotation and orienting the crystal so that an a-b face was perpendicular to the line of

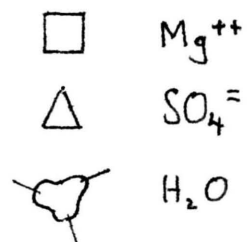
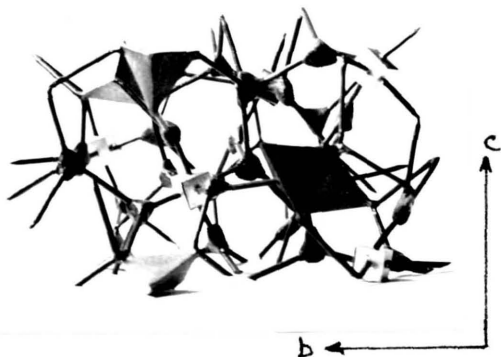
Figure 14 MODEL OF $MgSO_4 \cdot 7H_2O$ STRUCTURE



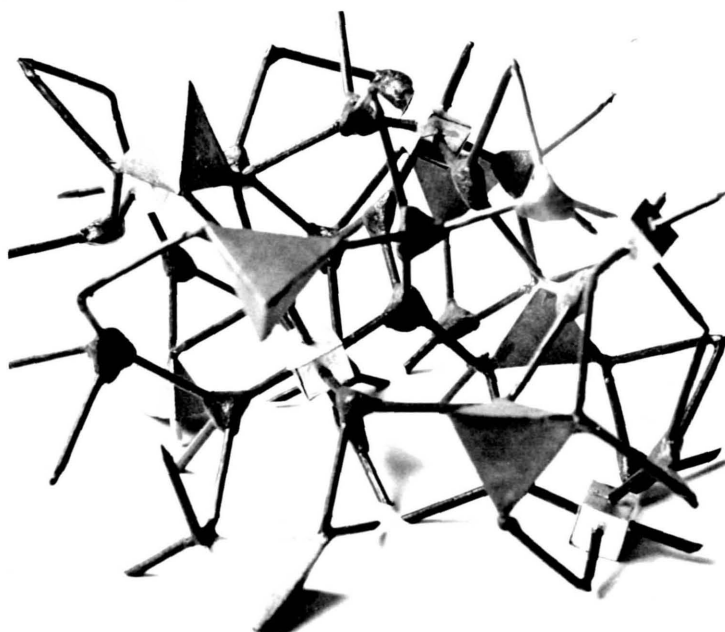
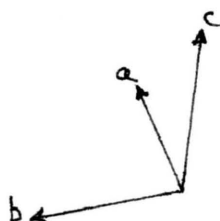
View along c axis



View along a axis



General View



sight of the travelling microscope. The width of the crystal (the distance between opposite a-b faces) was measured using a calibrated scale of 100 divisions, while growth in the c direction was measured simultaneously by lowering the microscope. These measurements required 10-30 seconds, and the rates obtained were adjusted to allow for growth occurring during this period. These corrections amounted to less than 5% in all but a few runs.

The solubility data²³ were sufficiently accurate for this work, error in the data being probably less than errors in concentration incurred in making up the solutions. Solutions were made up gravimetrically, using Analar salt and distilled water, and the concentrations were not checked by analysis. Otherwise the procedure was the same as with KBr.

A major requirement for determining the cause of breeding was a knowledge of the conditions at the crystal surface, which depend not only on the bulk supersaturation, but also on the rate of stirring. Because the growth rate of a crystal is presumably a function of the surface concentration only, the growth rate itself was used as a convenient independent variable. The phenomena described have in fact been related to the growth rate in the a-b directions in nearly all cases. Furthermore, an attempt has been made to determine the dependence of this growth rate on the surface supersaturation, so that the breeding phenomena may be related ultimately to supersaturation. These experiments are described in Appendix III.

II - NUCLEATION IN $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ SOLUTIONS

No extensive experiments were necessary to establish that spontaneous nucleation was not a factor in any of the breeding experiments. At 32.5°C , still solutions of 20°C supercooling could be maintained indefinitely without nucleation occurring. When ΔT was 26.5°C , hexahydrate crystals began to appear after 8 min. at 32.5°C . Supercoolings as high as 30°C were maintained overnight without nucleation, at room temperature.

Perspex models of crystals were rotated in highly concentrated solutions to determine at what point agitation would induce nucleation in the absence of a crystal. At 32.5°C and $\Delta T = 12.2^\circ\text{C}$ ($S = 1.108$), a model 0.52 cm. across was rotated at 1000 rpm for $2\frac{1}{2}$ hours without crystals appearing, the agitation ($Re = 590$) being five times greater than in any actual experiment. Increasing the agitation ($Re = 1700$) caused nucleation in 4 and 8 min. in other trials. When the supercooling was very high less agitation was required: at $\Delta T = 19.5^\circ\text{C}$, agitation equivalent to $Re = 180$ produced crystals, but these extreme conditions were never encountered in the actual experiments.

III - PRELIMINARY BREEDING EXPERIMENTS

(Using "untreated" seed crystals.)

In early experiments with aqueous $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solutions, it was found that the introduction of a crystal into a solution led to breeding of the same types as in the case of KBr. At even very

low supercoolings (less than $\Delta T = 1^{\circ}\text{C}$) crystals were observed to form and grow on the cell bottom. At higher supercoolings, needles often grew out from the seed as in Fig. 15, and when these became detached, e.g. when the crystal was rotated, many other crystals were usually formed.

Initial Breeding Effect

As in the case of the KBr investigations, it was concluded that the crystals which formed on the cell bottom were due to small crystal particles which fell from the seed when it was first introduced into the solution. The existence of such particles was again confirmed by the occasional growth of crystals from the supporting rod.

True Breeding and Splintering

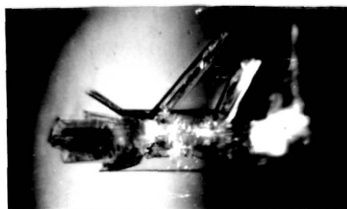
The breaking off of needle-like growths on stirring was analogous to the dropping off of irregular growths from the KBr crystals on stirring, and was followed by similar showers to those obtained with KBr. Thus these showers were attributed to splintering.

Neither of these phenomena were normally observed at low supercoolings, since needles such as those of Fig. 15 did not usually grow on unstirred crystals below about 7°C supercooling. At the higher supercoolings needles were very common, and it is thought that they were the result of some type of surface imperfection which heals over at low growth rates. This type of healing phenomenon has been noted by Egli and Zerfoss.²²

Figure 15 NEEDLES ON UNSTIRRED $MgSO_4 \cdot 7H_2O$

(a)

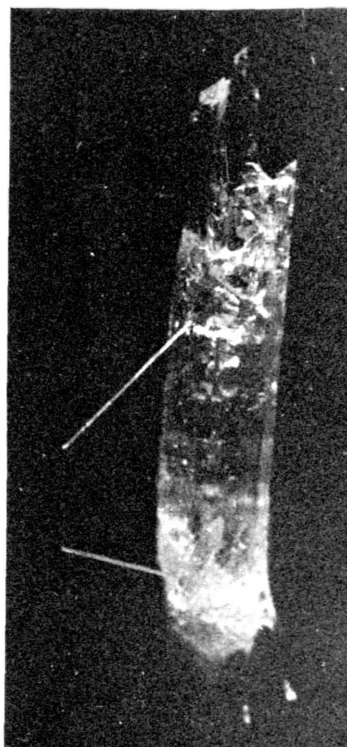
Grown at $20^{\circ}C$
($\Delta T \pm 10^{\circ}C$)
from untreated seed.



x 2.5

(b)

Grown at $32.5^{\circ}C$
($\Delta T \pm 12^{\circ}C$)
from a treated seed
which was allowed to
dry for 2 hours.



x 10

Attrition

Attrition was observed to be an important factor in producing new crystals when free crystals were present in the solutions. At supercoolings above 15°C , crystals falling through the solution adjacent to the cell walls left trails of crystals on the walls. The growth of needles into contact with the walls was also observed to produce new crystals, which grew loosely attached to the walls.

Evidence that collisions between crystals lead to the production of new nuclei is found in the fact that, once nuclei had been produced in agitated solutions, the rate of production of nuclei greatly increased. At supercoolings of about 10°C , complete crystallization, in the form of many thousands of tiny crystals, required only about twice the time required for the formation of the first few crystals. At supercoolings of about 7°C this factor was increased to about five.

Table 3 below summarizes some results from a later series. The times noted are t_1 , the time when the first new crystals were observed, and t_2 , the time when it was necessary to end the run because the free crystals obliterated the view of the seed crystal.

Table 3. Effect of Collisions ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)

Run	ΔT	Re	$t_1(\text{min.})$	$t_2(\text{min.})$
316	10.2	2.0	2	8
316	10.2	10.9	$2\frac{1}{2}$	6
316	10.2	30.2	$\frac{3}{4}$	$1\frac{1}{2}$
316	10.2	38.4	$\frac{3}{4}$	2
312	10.4	2.9	2	6
311	10.4	13.4	3	4
320	6.9	7.8	5	25
320	6.9	41.8	3	15

The effect of increased agitation (Re), which influences both the number and force of collisions, is also indicated by this table.

At low supercoolings, up to 4°C , the number of crystals initially formed was small (crystals only formed in a few runs) and hence the effect of attrition was diminished. However, it was rare when the formation of one free crystal did not lead to the later formation of at least a few more crystals. The fact of attrition is important in relation to the work of Ting and McCabe, who seeded their solutions with large numbers of free crystals. This is discussed fully in Chapter 5.

IV - PRETREATMENT OF SEEDS

Advantage has been taken of the healing effect described above to produce macroscopically perfect seed crystals for use in a more

detailed investigation of breeding. In the runs which are subsequently described, the following pre-treatment method was used to eliminate the initial breeding effect and the true breeding effect caused by the growth of needles from surface imperfections.

Small needle crystals of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (about 0.05×2.0 m.m.) were fixed axially on the support rod using Durofix adhesive, as before. They were then immersed in a slightly supersaturated ($\Delta T = 1-3^\circ\text{C}$) solution of aqueous $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ for about $\frac{1}{2}$ hour, to allow loose particles to drop off and surface imperfections to heal. Before immersion in the test cell, the support rod was washed well with distilled water to remove any further crystalline particles, and the seed crystal itself was also washed to prevent flawed growth due to cooling or evaporation.

The wet crystal was immersed and allowed to grow for a time before beginning to stir. Thus it was ensured that the inoculating crystals were free from both surface imperfections and small crystalline particles. The very few runs in which crystals subsequently developed attached to the rod, or in which needle-like growths appeared, were disregarded as far as breeding was concerned.

V - BREEDING RESULTS

(Treated seeds)

The results of many runs in which pre-treated crystals were rotated in nucleus-free solutions are summarized in tables 14, 15 and 16. The growth rates are the linear rates of advance in the

a-b (100 or 010) directions, and in the 001 or c direction. It should be noted that the {001} face was not usually evident and the latter growth rate is in fact the rate of advance of the intersection between pairs of {101} or {011} faces. Supersaturations have been reported as

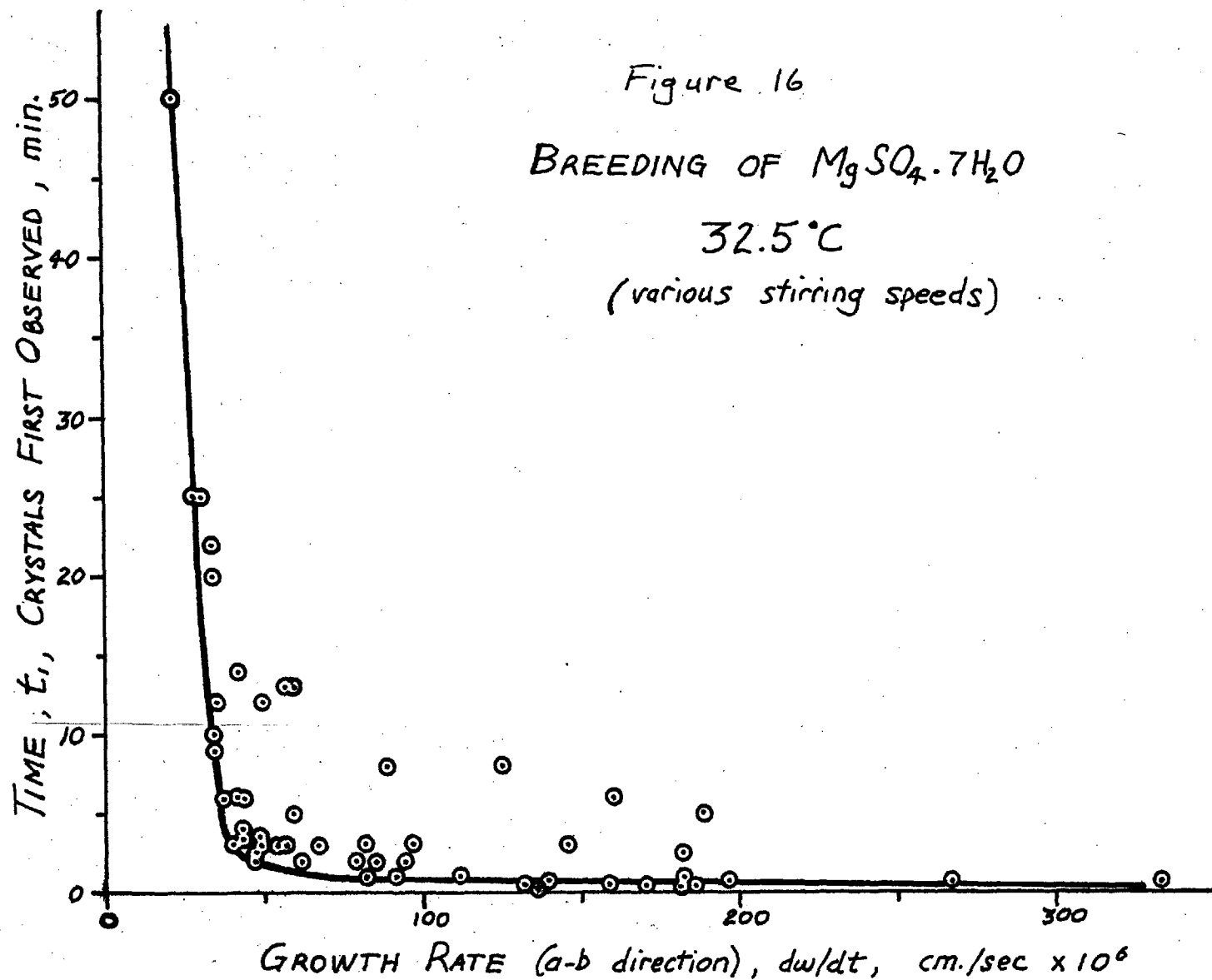
$$S = \frac{\text{actual mass fraction of Heptahydrate, } T}{\text{solubility, mass fraction Heptahydrate, } T}$$

The values of S, and of the crystal width (d) and length (l) reported, are the initial values when stirring was started. As with the KBr solutions, the growth rates were relatively constant through the duration of the run.

The appearance of the final crystals is designated as "good", "veiled" or "hollow", the meanings of these terms being discussed on p.76. In many runs, free crystals were observed in the body of the solution some time after the stirring was begun, and the time when these crystals appeared is reported in the tables as t_1 (minutes).

It is apparent from the tables that, when a clean crystal with a macroscopically perfect surface is rotated in a supersaturated solution, new crystals are often formed. The nature of this breeding process is revealed in two ways:

1) Examination of the tables shows an almost 1:1 correspondence between flawed ("v" or "h") growth and the occurrence of breeding: when good crystals were produced, breeding did not occur, but when the crystals were flawed, breeding almost always occurred. Thus the breeding process is either caused by the flaws themselves, or by the mechanism which produces the flaws.

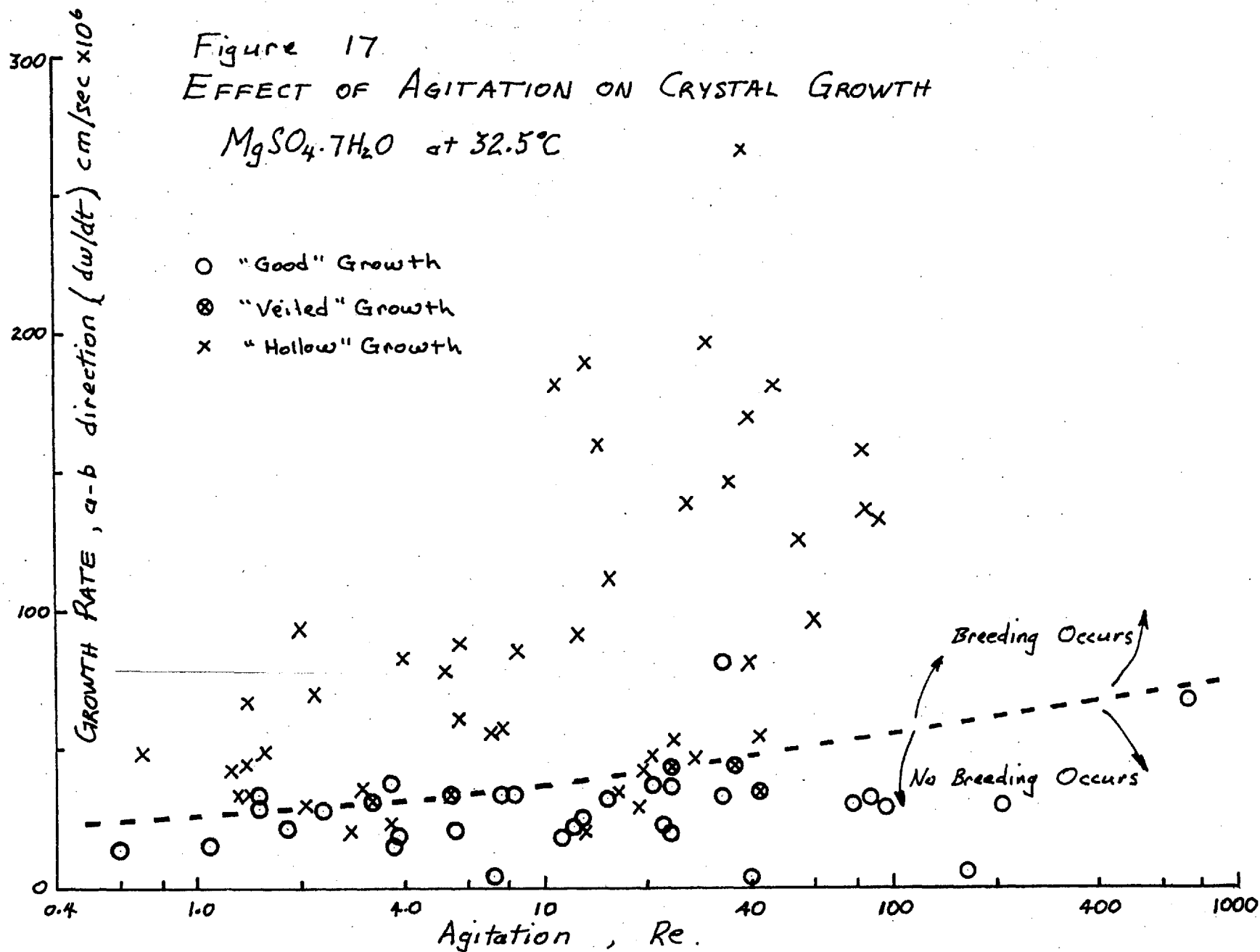


2) When breeding occurred, the time required for the nuclei to form and grow to visible sizes was related to the surface supersaturation as indicated by the measured growth rates. Fig. 16, which is for rotated crystals at 32.5°C , indicates the form of the relationship: breeding occurs slowly, if at all, when the crystal grows at less than 20×10^{-6} c.m. / sec. in the a-b directions, and it occurs rapidly when the surface supersaturation is such as to yield growth rates in excess of about 35×10^{-6} c.m. / sec.

Although, therefore, the appearance of breeding can be related primarily to the a-b growth rates (and thence to the true surface supersaturation), nevertheless the independent effect of stirring is not negligible. Thus Fig. 17 shows the a-b growth rates obtained as a function of agitation (as measured by the initial Reynolds Number, see table 22). The forms of the crystals obtained have been indicated by the use of different symbols, and, because of the above noted relationship between flawed growth and breeding these symbols may also be interpreted as indicating whether or not breeding occurred.

It can be seen in Fig. 17 that two regions exist, separated by a fairly well defined line, in one of which (the upper) breeding is to be expected, while in the other breeding will not occur. Since the line is not horizontal it is clear that, when the agitation is very great, breeding does not occur until the growth rate is considerably greater than the necessary value at low rates of agitation.

Figure 17
EFFECT OF AGITATION ON CRYSTAL GROWTH
 $MgSO_4 \cdot 7H_2O$ at $32.5^\circ C$



In order to explain this, and to determine the mechanism of the breeding process, it is necessary to discuss the occurrence of the growth flaws which accompany breeding.

VI - GROWTH OF $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

As in the case of KBr, the growth rates of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ from aqueous solutions have been found to be partially controlled by the rate of diffusion of solute to the crystal faces. Fig. 18 shows the effect of stirring on the growth rate of crystals at high supercoolings. The stirring has been measured by the relative velocity between the crystal edge and the solution, as in the case of the similar results for KBr.

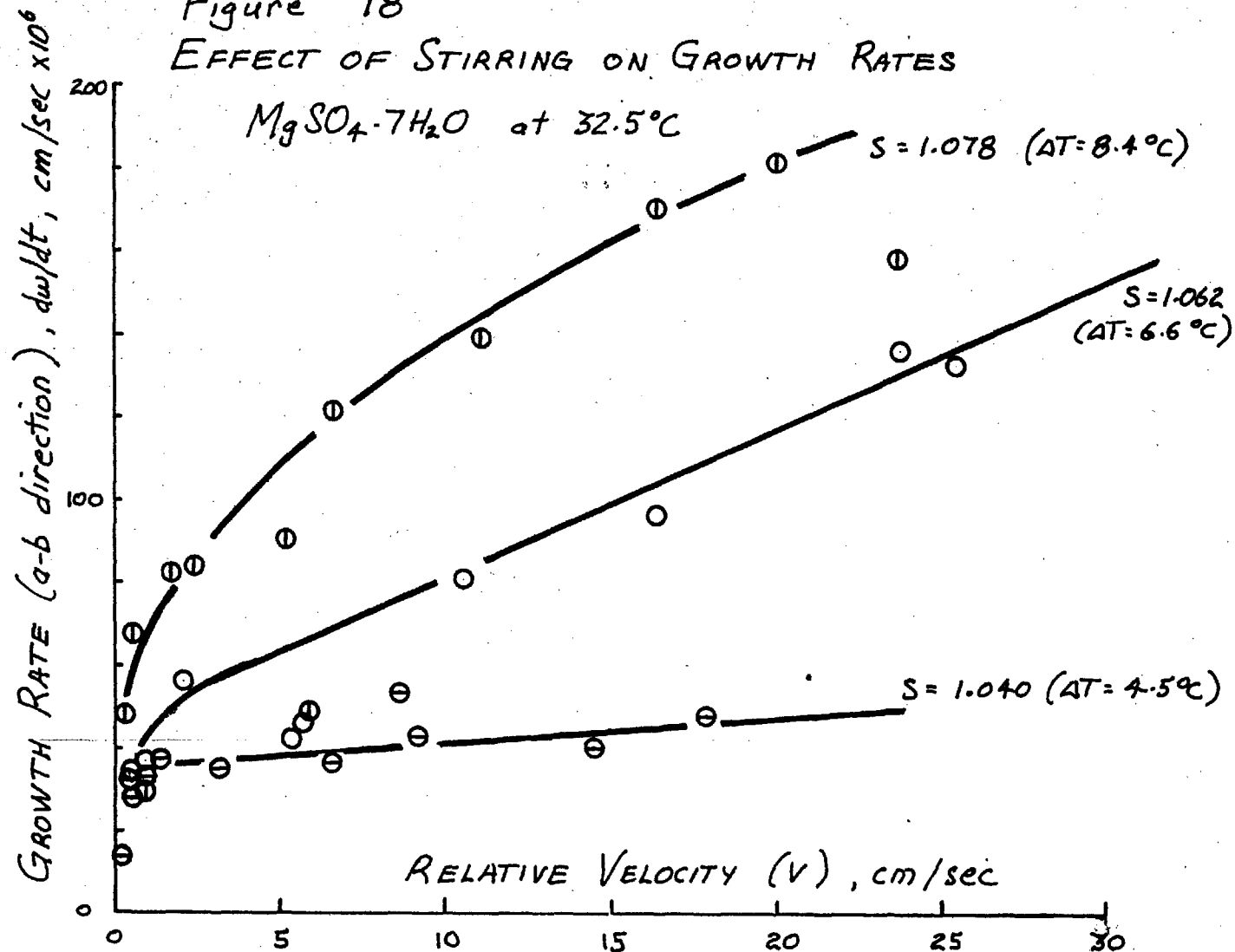
Even at a supercooling of only $4\frac{1}{2}^\circ\text{C}$, Fig. 18 indicates that the diffusional barrier was not eliminated by vigorous agitation (rotation of the crystal at over 3000 rpm). At greater supercoolings the maximum growth rate was not nearly approached. At supercoolings below $3\frac{1}{2}^\circ\text{C}$, on the other hand, it was possible largely to eliminate diffusional effects by stirring more vigorously, and this fact has been used to permit a determination of the dependance of the growth rate on surface supersaturation (Appendix III).

It has been argued³¹ that the fact that growth in the c-direction occurs at greater rates than the a-b rates shown in Fig. 18 (see table 14), is proof that diffusion is not a factor. Diffusion, it is said, cannot differ from face to face. However, this argument applies only where growth is good, since the relation

Figure 18

EFFECT OF STIRRING ON GROWTH RATES

$MgSO_4 \cdot 7H_2O$ at $32.5^\circ C$



between mass flux and the linear growth rates measured here is indefinite when inclusions of solution are a factor.

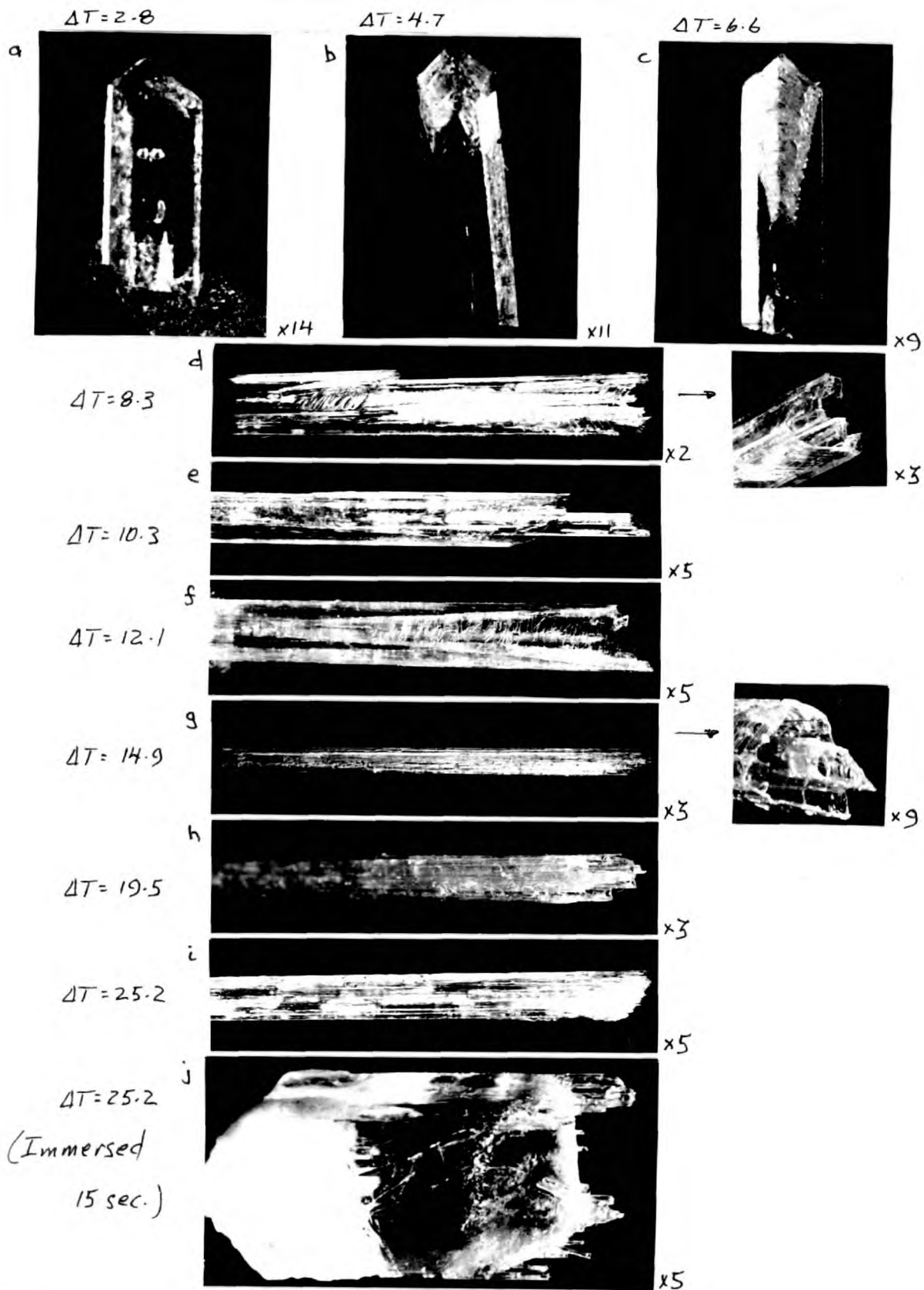
Examination of table 14 indicates that the ratio of the growth rates in the c and a-b directions has a maximum value of about 30 (run 409) whereas the work on highly agitated solutions at low supercoolings (Appendix III) would lead us to expect a maximum ratio of about 2.5. This large discrepancy is also due to the occurrence of inclusions of solution, and necessitates a description of the quality of the crystals obtained.

Quality of Growth

Fig. 19 shows a series of photographs of crystals of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ grown from still solutions at 32.5°C , with increasingly higher supercoolings. Up to supercoolings greater than 3°C the crystals were perfectly transparent and very well developed. At supercoolings approaching 5°C , a slight depletion veil developed, the cloudiness being caused by inclusions of solution. The veil became more pronounced, and at supercoolings of about 8°C an essentially hollow crystal was produced, depleted solution being trapped by the growth which occurred around it. With still greater supercoolings the development of spikes occurred ⁱⁿ the hollow section of the crystal, these spikes being in effect further hollow crystals.

As the supersaturation approached very high values, the number of hollow spikes increased and their size diminished, so that at $\Delta T \approx 26^\circ\text{C}$, the crystal was a series of long, thin, inter-connected cells full of solution and running the entire length of the crystal.

Figure 19

UNSTIRRED $MgSO_4 \cdot 7H_2O$ 

At the higher supercoolings, the tendency for the crystal to "broom" out is noticeable in the photographs - the fast growing crystal end widening more quickly than the portion near the original seed.

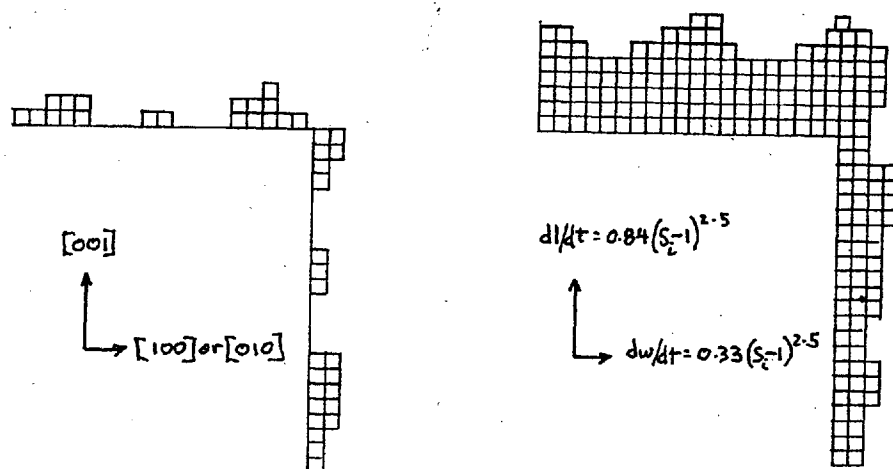
Fig. 19j, a photograph of a crystal immersed for 15 sec. in a solution at $\Delta T = 26.5$, shows the initial stages of development of a hollow crystal. Fig. 20 indicates the probable mechanism whereby imperfect growth occurs and inclusions are formed. When the distribution of solute over the crystal surface is even, as at low supercoolings or with a highly agitated solution, small degrees of roughness which may arise at the crystal surface are of no importance, and good growth occurs (Fig. 20a).

When a significant concentration gradient exists near the crystal surface, however, (Fig. 20b) the tips of any projections may come into contact with more concentrated solution and therefore tend to extend themselves at the expense of complete growth. Such a concentration gradient could arise due to the presence of a diffusion barrier in insufficiently agitated solutions. It is of course necessary to postulate the small scale surface roughness necessary for this mechanism, but this is a common postulation.^{32, 33} Similar mechanisms for the growth of dendrites have been proposed by Lawson and Nielsen³⁴ and many other authors.

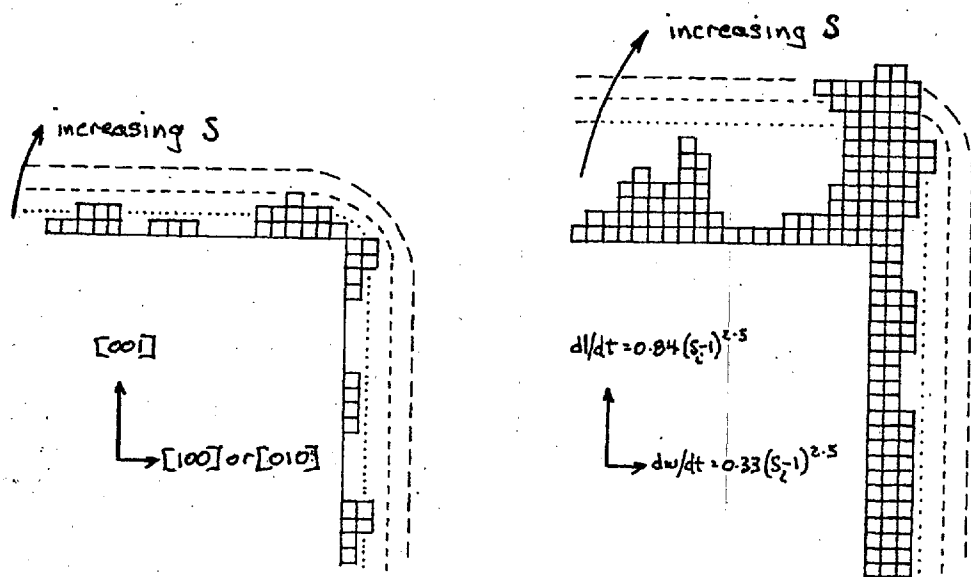
If such a diffusional effect is responsible for the observed flawed growth, it also explains why the flaws are observed to occur in the c-direction and not in the a-b directions, since the degree of diffusion control would be greater for the faster-growing direction (i.e. the c direction, for which K_R is 2.6 times the reaction rate

Figure 20
EFFECT OF SURFACE ROUGHNESS ON CRYSTAL GROWTH

(a) - highly agitated crystals - uniform supersaturation



(b) - insufficiently agitated crystals - variable supersaturation



constant in the a-b directions). Such an explanation also permits the relationship of Fig. 17 to be understood: at high rates of agitation, more perfect crystals would be expected at relatively higher growth rates, due to the decrease in the proportion of diffusional control. That diffusional effects are at least partly responsible for growth imperfections is further illustrated by run 310. In this run, with a bulk supercooling of 3.9°C , the unstirred crystal was veiled ($dw/dt = 6 \times 10^{-6} \text{ c.m./sec.}$) whereas the stirred crystals were good, with no inclusions (dw/dt up to $33 \times 10^{-6} \text{ c.m./sec.}$).

Nevertheless, it was not possible to eliminate diffusional effects at higher supercoolings, as Fig. 18 has shown, and hence veiled and hollow crystals were not unusual in stirred solutions above about $4\frac{1}{2}^{\circ}\text{C}$ supercooling. Some of the crystals obtained were photographed and are shown in Fig. 21. It is interesting to note that occasional spiral growths were obtained (Fig. 21a,b), although these were not reflections of any spiral lattice structure.

Ratio of Growth Rates

The effects of agitation on the diffusion boundary layer can also be studied by examining the ratio of the growth rates in the c and a-b directions. As has been mentioned (p.76), measurements at lower supersaturations and at high rates of agitation would lead us to expect values of this ratio between 1 and 2.6, yet much higher ratios were obtained. The occurrence

Figure 21 STIRRED GROWTH OF $MgSO_4 \cdot 7H_2O$

Run 309
 $\Delta T = 3.9$, 50rpm



x14

Run 410
 $\Delta T = 8.4$ 40rpm



x5

Run 327 (45°C)
 $\Delta T = 6.1$, 50rpm



x4

$\Delta T = 6.6$

42rpm



Run 393

x6

660 rpm



Run 397

x5

$\Delta T = 8.4$

280 rpm



Run 399

x5

500 rpm



Run 409

x7

1100 rpm



Run 406

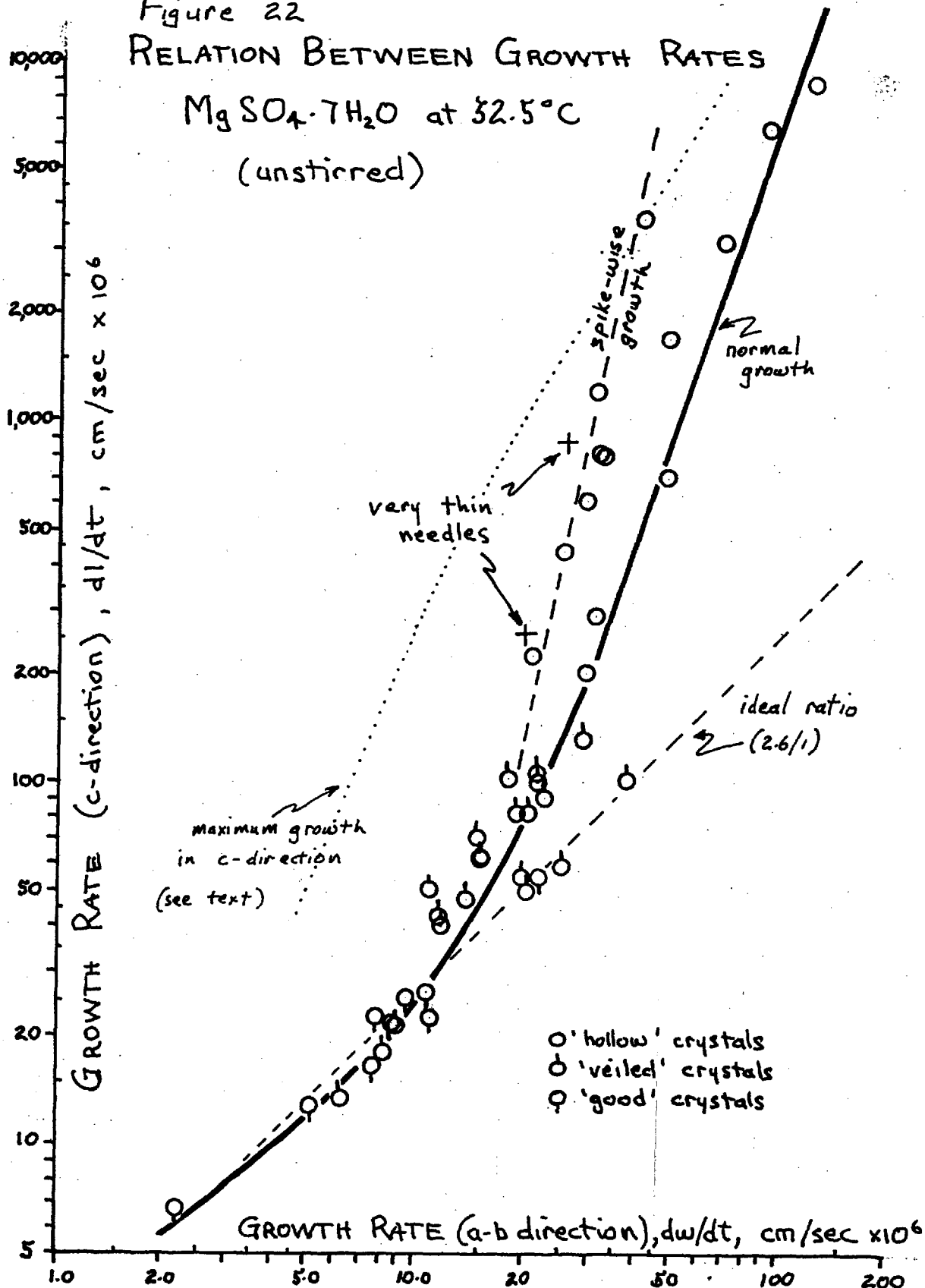
x3.5

of these higher ratios was said to be due to the presence of inclusions of solution. That this was the case will be shown by a study, first of the stationary crystals, and then of the agitated ones.

Fig. 22 shows the relation between the c and a-b growth rates for unstirred $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ crystals, and the growth forms of the crystals obtained. The lower dashed line of this graph represents the relation which would be expected if diffusion were not a factor (i.e. if the supersaturation were the same at all crystal surfaces) and is based on the work described in Appendix III. It can be seen that at low supercoolings (yielding growth rates below 15×10^{-6} c.m./sec. this relation holds well, but at higher supercoolings there is a tendency towards proportionately higher c-direction rates, i.e. higher growth rate ratios. It can also be seen that the deviating crystals were veiled or hollow, the hollow crystals deviating more than the veiled crystals. It seems likely that the distance above the "ideal" curve can be considered a measure of the amount of solution included.

In some of the runs at high supercoolings, notably runs 425-7 (see table 17), two growth rates in the c direction were measurable. The higher of these rates in every case represented the growth of small spikes which grew in advance of the main crystal (as in Fig. 21). In each case the spike grew rapidly for a time, and then, seemingly after attaining a certain thickness, slowed to the rate of the main crystal. The growth

Figure 22
RELATION BETWEEN GROWTH RATES
 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ at 32.5°C
(unstirred)



rates of the main crystal are shown by the solid line in Fig.22, those of the spike-wise growth by the dashed line so labeled.

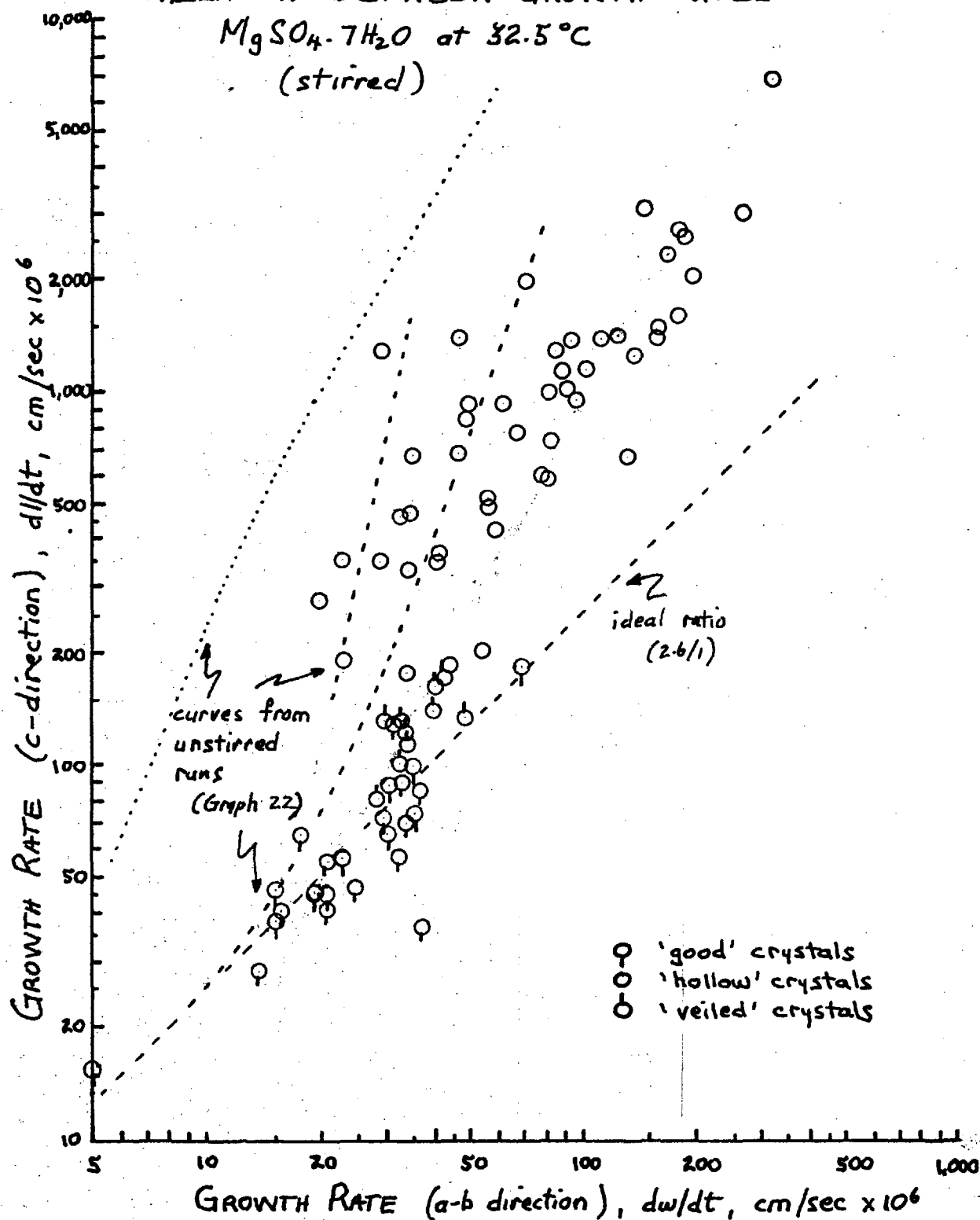
It is also possible to estimate a maximum curve for spike-wise growth, corresponding to a needle growing normally (or not at all) in the a-b directions, with partial diffusional control, but growing in the c direction at the maximum rate permitted by the bulk supersaturation. Values of S, corresponding to specific values of the a-b rate, have been estimated from graph 30 (Appendix III) and these used to calculate the maximum c direction rates from the relation derived in Appendix III:

$$dl/dt = 0.841 (S - 1)^{2.5}$$

The curve thus obtained appears on graph 22 as a dotted line, and indicates the maximum possible c direction growth rate for any given bulk supercooling (here measured by the corresponding a-b growth rate). The c direction growth rates of two very thin (non-thickening) whiskers which were observed, are also shown on the same basis.

Fig. 22 suggests that, at very high supersaturations, spike-wise growth occurs in the c direction at very nearly the maximum possible rate. It also confirms the observation (p.76) that at very high supersaturations, the "normal" unstirred growth form resembled a bundle of very small needles. At supercoolings less than about 7°C (the value corresponding to an unstirred a-b growth rate of 20×10^{-6} c.m./sec.,) spike-wise growth does not occur, although veiled growth may occur at much lower supercoolings.

Figure 23
 RELATION BETWEEN GROWTH RATES
 $MgSO_4 \cdot 7H_2O$ at $32.5^\circ C$
 (stirred)



In order to judge the effects of agitation on the ratio of the growth rates, the curves from Fig. 22, for unstirred solutions, have been super-imposed on the stirred results in Graph 23. Again the a-b growth rates should be thought of as a measure of the surface supersaturation. It can be seen that, in general, the effect of agitation has been to decrease the ratio of the growth rates: the great majority of points in graph 23 lie below the normal growth curve of Fig. 22. (This is a reflection of the fact that the c direction growth rates are diffusion controlled to a greater extent than the a-b rates.) It is also clear that the c direction rates do not approach their maximum possible values as closely as in unagitated systems.

In the case of stirred crystals, Fig. 23 also indicates a much wider range of surface supersaturations (a-b growth rates) over which either good or flawed growth could occur. At high rates of agitation (see also Fig. 17,) growth irregularities could apparently be eliminated, although the growth rate might be such as would produce flaws if the same rate were the result of a higher bulk supersaturation with a lower rate of agitation. The fact that growth flaws did not necessarily arise at high growth rates is a further indication that the flaws were not solely due to some sort of internal imperfection (or dislocation) which arises or becomes evident at high growth rates. Rather, it is felt that the presence of a diffusional barrier (giving rise to concentration gradients) is also a factor, and that the mechanism described previously would explain these observations.

VII - BREEDING MECHANISM

The mechanism of the breeding process can therefore be described. When, due to the existence of a significant diffusion barrier, small scale surface roughnesses come in contact with more concentrated solution than surrounding portions of the crystal surface, flawed growth may arise in the c direction. These flawed growths resemble needles in many respects, and are not observed at a-b direction growth rates below about 20×10^{-6} c.m. / sec.

Not only does this type of growth lead to inclusions of solution, but, if there is agitation of the solution some of the growths may be broken off and swept into the solution, forming new nuclei. Thus the process responsible for the nuclei in these cases is a "true" breeding process. As is discussed in Chapter 5, it is believed that breeding due to this mechanism may account for the second supersolubility curve found by Ting and McCabe.

Chapter 5

CONCLUSIONS & DISCUSSION

The present experiments indicate that breeding in the solutions examined may be due to any or all of three separate mechanisms besides the trivial case of the introduction of nuclei along with the seed. It is believed that the only other quantitative studies so far conducted, those of Ting and McCabe, and of Heubel and Devrainne, can also be explained by these mechanisms. Each mechanism will be discussed separately in order to summarize the data supporting it.

I - ATTRITION

Nuclei have been observed to form in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and KBr solutions due to impacts between crystals and the cell walls, which are believed to break off small crystal particles. The rapid production of nuclei which occurred in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solutions as soon as free crystals appeared probably was mainly due to attrition, although splintering (discussed below) may also have been a factor. The effects of attrition were much greater at high supercoolings, but it is probably an important factor even at very low supercoolings.

Attrition was not normally observed at less than 4°C supercooling in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solutions, simply because free crystals were only very occasionally formed at such supercoolings. The very fact that it was possible to eliminate breeding at low super-

coolings is a strong indication that the initial breeding effect observed by Ting and McCabe (at supercoolings as low as $\frac{1}{2}^{\circ}\text{C}$) was due entirely to attrition, since the major difference between their experiments and the present ones was the presence in their solutions of large numbers of free crystals. In the present work, the seed crystals were prevented from touching the walls and it was necessary for some true breeding effect to produce free crystals before attrition could be considered a factor.

Thus, although McCabe has recognized that attrition and impacts may be factors in breeding¹, he appears to have underestimated their importance. It is not possible to distinguish the effects of attrition from those of other breeding mechanisms in his experiments.

It is also very likely that the initial breeding effect of Heubel and Devrainne was due to attrition.

It was not possible to distinguish any effect of attrition from the possible effects of splintering in the case of the work on Zn - Hg. However, it was concluded that significant amounts of attrition did not occur when the supercooling was less than 0.1°C .

II - SPLINTERING

In the work on KBr and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solutions, it was observed that the breaking off of dendrites or needles often produced large numbers of nuclei. These appeared within a few seconds in the region of the seed crystal. The apparent explanation of these

crystals is the production of a great many very small crystal fragments, or splinters, due to the fracturing of the projection.

This same explanation was offered by Brewer and Palmer²⁸ to explain a similar phenomenon occurring in cloud chambers. Under certain conditions of supersaturation of water vapour they observed that, when ice crystals on the walls of the cloud chamber broke loose and fell (presumably because of thermal shock or vibrations,) a trail of extremely small ice crystals quickly appeared in that region of the chamber. These crystals grew rapidly and settled out, and were not responsible for further breeding. Brewer and Palmer described these crystals as being due to "splintering" and it is believed that the crystals described in the present experiments were due to the same phenomenon.

Since a great range of sizes of splinters would be produced by this type of process, and since the size of particle which will grow in a supercooled solution is a function of the supercooling, a dependence of the number of nuclei on the supercooling would be expected. This has been qualitatively observed in the case of KBr. Such a dependence was also observed in the Zn - Hg experiments, and it is possible that splintering was the source of the many small crystals observed in that system. It is not possible to eliminate attrition as the source of these crystals, however, since a similar dependence of numbers on supersaturation might be expected in that case as well.

The observation of nucleus formation due to splintering in such varying systems as those noted suggests that it is a very widely occurring phenomenon. This is not surprising, since it would seem to be based on the brittleness of crystalline materials. On the other hand, since large dendritic growths, needles, or some other unusual growth form would seem to be necessary for it to occur, the practical implications of splintering may not be great.

III - TRUE BREEDING

Besides the two types of breeding already noted, which seem to depend only on mechanical effects, a possibly more fundamentally important type of breeding has been found. This consisted of the growth and detachment of spikes, needles, or dendrites to form nuclei. Forms of this phenomenon occurred in all the solutions investigated here, preceding the occurrence of either splintering or attrition in each case. The "false graining" described by Van Hook (p. 18) seems to be a combination of this "true" breeding with the resultant splintering and attrition.

It is difficult to generalize about the origins of the irregular growths which are responsible for breeding in solutions, since the mechanisms of their formation appeared to be different in each case. Thus it was possible to eliminate these growths in the case of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ by growing the crystals at low supercoolings, yet this was not possible with KBr. The necessary low growth rates for such healing with KBr may exist, but if so they are very small. It

It would seem, however, that the probable prerequisites for the occurrence of irregular growth are:

- 1) Some sort of surface feature
- 2) Relatively high supersaturations.

In addition, the existence of a concentration gradient near the crystal surface should make the occurrence of irregular growth more likely.

The explanation of Powers for his results with aqueous sucrose solutions at low supercoolings can possibly be considered a form of true breeding. He postulated that (invisible) nuclei were shed from the growing seed when it was rotated at high speed, and it seems that the only difference between this concept and that above lies in the size of the particles shed from the seed. Evidence that invisibly small particles may be shed from vigorously agitated KBr crystals was found in the present experiments, in which it is known that the growth forms were by no means good. There is also a great deal of evidence that very small needles may be shed from growing $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ crystals.

In this case breeding was very strongly associated with flawed growth (inclusions) along the $[001]$ axis of the crystals, and both the inclusions and the breeding were found to result from irregular growth which arose due to the presence of a diffusion layer. Because growth was partially diffusion controlled, irregularities on the $[001]$ faces came in contact with more concentrated solution and hence grew more quickly.

Some of the needles thus formed were broken off and swept into the solution by the agitation, forming new nuclei.

Butler³¹ has discussed the effect on the growth rate of inclusions similar to those obtained here and concluded that the effect was due to the presence or formation of some sort of "dislocation". It is felt that this is an incorrect and misleading use of the term dislocation, and that his results are explainable on the basis of partial diffusional control of the growth rates.

Heubel and Devrainne have also suggested that the breeding they observed may have been due to an increase in the number of "dislocations" in a crystal as it grows more quickly. This, they say, would explain why there appears to be a critical size, dependent on the supercooling, below which a crystal of KNO_3 will not breed new crystals^{19,34}. Again it is felt that this use of the word dislocation may be misleading, since a size effect similar to the one they note, might also be due to purely diffusional effects.

In fact, the size effect which they describe appears to be the common observation² that it becomes more difficult to produce a perfect crystal as the crystal size increases. Egli and Zerfoss²² have said that there appears to be no reason to expect such a size effect, and it may be that the observed effects are partly due to the difficulty of distributing solution evenly over a crystal face where diffusion is a factor. The work of Heubel and Devrainne has thus far been

carried out at only one stirring rate, however, and it is impossible to estimate whether diffusion is a factor in their work.

In the case of the work of Ting and McCabe on $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, which yielded results similar to those of Heubel and Devrainne, the initial breeding phenomenon has already been shown to be due to attrition. It is believed that Ting and McCabe's second breeding phenomenon can be shown almost certainly to be due to the true breeding mechanism studied in the present work. Table 5 below shows the result of ^{extrapolating} their data at 146 rpm stirring to 32.5°C , the temperature of the present runs. (t_2) is the time at which the second nucleation of crystals was observed, and ΔT_2 the supercooling at that time.

Table 5 RESULTS OF TING & McCABE¹⁶ ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$)

Cooling Rate, ($^\circ\text{C/hr.}$)	ΔT_2 , ($^\circ\text{C}$)	t_2 (min.)
6.0	3.9	39
3.6	3.5	60
2.4	2.8	69

It can be seen that the supercooling at which crystals appeared changed but little with cooling rate at high cooling rates. If the solutions had been inoculated at a constant supercooling of just over 4°C , nuclei would be expected in times very similar to those obtained in the present work,

i.e. 10 - 30 minutes. It is, of course, impossible to relate the effects of stirring in Ting and McCabe's work to those in the present work. However, it seems clear that their breeding results can be explained on the same basis as those in the present experiments on $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

IV - CONCLUSIONS

The production of nuclei in solutions where seed crystals are present, is due to three mechanisms.

- 1) Attrition - impacts between the seeds and either themselves or the vessel walls causing small particles to be broken off from the seeds.
- 2) True Breeding - the detachment of irregular growths (needles or dendrites) which may grow from the seeds.
- 3) Splintering - the production of crystal fragments or splinters when true breeding occurs.

The results of Ting and McCabe (and possibly those of Heubel and Devrainne) can be explained by these mechanisms. Their first new crystals were formed by attrition. True breeding, the irregular growths being partly the result of partial diffusional control of growth in the $[001]$ direction, was responsible for the initiation of the second nucleation effect, after which splintering and/or increased attrition probably produced even more nuclei.

Appendix I

Zinc Mercury Amalgams

Contents:

1. Nucleation Calculations	p. 100
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TABLE 6

ZN - Hg, SUMMARY OF COOLING RUNS (Stirred)
(without added crystals)

RUN No.	T _S °C	Cooling Rate °C/hr.	Max ΔT °C	Max S
52	27.3	1.95	2.1	1.051
74	30.3	1.10	1.25	1.030
76	30.3	4.0	2.58	1.063
102	33.5	5.4	3.0	1.073
103	33.5	3.7	3.1	1.075
111	32.8	4.6	2.9	1.071
112	32.8	1.7	2.6	1.063
113	32.8	1.4	2.0	1.049
115	32.8	1.4	1.4	1.034
145	34.9	1.8	1.9	1.046
146	34.9	2.2	2.2	1.054
149	34.9	2.0	1.8	1.044
150	34.9	1.8	1.7	1.041
153	34.9	1.7	1.5	1.036
136	36.0	2.9	1.4	1.034
138	36.0	2.0	1.4	1.034
157	36.9	2.1	1.9	1.046
158	36.8	1.9	1.5	1.036
159	37.2	2.1	1.7	1.041
160	37.2	3.9	2.5	1.061
161	36.9	2.5	2.0	1.049
165	36.8	2.0	1.7	1.041
166	36.8	2.2	1.7	1.041
168	36.8	2.3	1.8	1.044
174	36.5	2.6	1.9	1.046
176	36.5	1.8	1.0	1.024
179	36.5	2.9	2.2	1.054
187	35.6	5.3	2.2	1.054
188	35.6	2.8	1.9	1.046
196	34.8	3.4	2.2	1.054
198	27.3	1.5	1.4	1.034
199	27.3	1.3	1.4	1.034
201	27.0	1.2	1.2	1.029
202	27.0	0.3	0.95	1.023
205	24.7	1.0	1.6	1.039
206	24.7	0.25	0.85	1.021
209	27.5	0.71	1.2	1.029
210	27.5	0.25	0.65	1.016
212	27.5	0.50	1.1	1.027
213	27.5	0.25	0.85	1.021
218	26.9	8.9	4.3	1.105

TABLE 6 (continued)

ZN - Hg - Summary of Cooling Runs (Stirred)

RUN No.	T _s	Cooling Rate	Max ΔT	Max S
219	26.9	3.00	1.60	1.024
220	26.9	1.07	1.45	1.035
221	26.9	0.25	0.97	1.024
222	26.9	0.50	1.1	1.027
223	26.9	0.125	0.71	1.017
227	26.9	0.50	1.18	1.029
239	26.3	0.50	1.2	1.029
245	28.4	0.50	0.80	1.019
250	24.1	0.50	0.80	1.019
257	27.5	6.0	2.0	1.049
262	27.4	0.50	0.80	1.019
265	27.4	0.50	0.80	1.019
266	27.4	0.25	0.50	1.012
267	27.4	0.25	0.60	1.015
268	27.4	0.25	0.50	1.012
269	27.4	0.25	0.70	1.017

Unstirred Runs

50	27.5	2.5	2.8	1.068
207	24.0	0.25	0.75	1.018
208	24.0	0.25	1.0	1.024
238	26.3	0.50	1.6	1.039
246	28.4	1.0	1.9	1.046
248	25.0	2.0	2.0	1.049
249	25.0	1.2	2.0	1.049
255	27.5	0.25	0.70	1.017

TABLE 7

Constant Temperature Runs, Stirred

Run N ^o	T _s	Supercooling $\Delta T, ^\circ\text{C}$	Supersat S	t hours
75	30.3	1.0	1.024	1.5
87	33.5	1.2	1.029	1.6
88	33.5	1.8	1.044	0.6
89	33.5	1.7	1.041	0.5
91	33.5	1.8	1.044	0.5
92	33.5	1.6	1.039	1.3
94	33.5	1.8	1.044	0.3
95	33.5	1.6	1.039	1.0
96	33.5	1.4	1.034	1.2
97	33.5	1.3	1.032	1.5
98	33.5	1.5	1.036	1.0
99	33.5	1.1	1.027	3.2
101	33.5	1.3	1.032	1.7
104	33.5	1.0	1.024	5
137	36.0	1.4	1.034	0.2
139	36.0	1.0	1.024	0.8
140	36.0	0.75	1.018	0.8
141	36.0	0.75	1.018	1.3
147	34.9	1.1	1.027	0.9
152	34.9	0.50	1.012	2.8
162	36.8	1.0	1.024	0.6
163	36.8	0.8	1.019	1.0
164	36.8	0.5	1.012	2.5
183	36.5	0.7	1.017	0.8
184	36.5	0.5	1.012	2.0
190	35.6	1.1	1.027	0.2
211	26.9	0.30	1.0073	13
215	26.9	0.35	1.0085	9
224	26.9	0.74	1.018	4.6
228	26.9	0.60	1.015	5.3
229	26.9	0.49	1.0119	7.0
230	26.9	0.35	1.0085	8 $\frac{1}{2}$
240	26.9	0.45	1.011	1.9
241	26.9	0.30	1.0073	8
242	26.9	0.20	1.0049	8

1. Nucleation Calculations

The results of the constant temperature runs summarized in table 7 were used to estimate the nucleation rates, using Holloman and Turnbull's equation (3) for homogeneous nucleation in metals. Values of σ were first estimated from plots of $\log_{10} I$ vs $(1/\Delta T)^2$, which yielded straight lines, the approximate slope of which can be represented by

$$\text{Slope} = - \frac{16 \pi T_0^2 \sigma^3}{3 \times 2.3 (\Delta H)^2 kT}$$

For the purpose of this estimate, the relative nucleation rates were taken as being inversely proportional to the nucleation times given in table 7. Benjamin and Strickland-Constable have carried out a similar estimation using $t_{0.4}$, the time required for 40% crystallization, but there is no particular advantage in their method. The slopes of the lines obtained are given in table 23 below, along with the calculated values of σ . The physical constants used were

$$k = 8.30 \times 10^7 \text{ erg/gm mole } ^\circ\text{K}$$

$$\Delta H = 2250 \text{ cal/gm mole }^{24}$$

Table 23 Estimation of σ

T (°K)	Slope	σ
300	-11.0	4.0
300	-12.4	4.1
307	-0.72	1.6
309	-1.73	2.1
310	-7.25	3.4
		3.0 Average

By substituting the average value of σ back into equation (3) it was possible to estimate the nucleation rate at various supercoolings for the typical case of an amalgam saturated at 300°K. The activation energy for diffusion of zinc in mercury has been taken to be the same order of magnitude as that for the self diffusion of mercury³⁶:

$$\Delta g = 1160 \text{ cal./gm. mole}$$

The concentration of the solution has been taken as 0.0081 gm moles Zn/cc of solution.

Using these values, the frequency factor

$$\left[\frac{N k T}{h} \right] = 3 \times 10^{34} \text{ nuclei/sec.c.c.}$$

and the diffusion term is

$$\exp. \left[\frac{-\Delta g}{kT} \right] = 0.14$$

TABLE 8 Nucleation Calculations for Zn - Hg

Supercooling $\Delta T, ^\circ\text{C}$	Supersat'n S	Nucleation Time (sec/nucleus)	r^* cm $\times 10^7$	n^* <u>molecules</u> nucleus
0.1	1.0025	$10^{44.5}$	9.2	207000
0.2	1.0049	10^{85}	4.7	27700
0.3	1.0073	10^{18}	3.2	8500
0.33	1.0080	10^9	2.9	5500
0.34	1.00825	10^6	2.8	5900
0.35	1.0085	10^4	2.7	5400
0.36	1.00875	10^2	2.6	4900
0.37	1.0090	1.0	2.6	4510
0.38	1.0092	10^{-2}	2.5	4250
0.39	1.00945	10^{-3}	2.5	3900
0.4	1.0097	10^{-5}	2.4	3600
0.5	1.0121	10^{-16}	1.9	1900
0.6	1.0146	10^{-22}	1.6	1100
0.8	1.0194	10^{-28}	1.2	500
1.0	1.0243	10^{-30}	1.0	250
2.0	1.0486	10^{-34}	0.5	30

The calculation of nucleation time ($1/I$, sec./nucleus) for a typical amalgam is shown in table 8. This table also includes values of the radius and size of a critical nucleus, based on equation (4), and using the same average value of σ .

Table 8 indicates that a very rapid increase in nucleation rate occurs at a supercooling of $0.35 \pm 0.38^\circ\text{C}$. A practical value for the metastable limit would be about 0.34°C , since at this value it takes about 300 hours for a nucleus to form.

The value of σ obtained here, 3.0, was approximately the same as that found by Benjamin and Strickland-Constable (3.4), indicating the possibility that the metastable limit in their work was of the same order. The importance of this in relation to their discussion of breeding is mentioned in the body of the thesis (p. 36).

It must be noted that the actual number of nuclei formed in the one experiment where spontaneous nucleation was measured (197) bore no relation to that calculated in table 8. Thus, while 1700 nuclei/cc were found ($\Delta T = 2.0^\circ\text{C}$), the Holloman-Turnbull theory predicts the formation of 10^{34} nuclei/c.c.sec. It is evident that even if, in spite of Kuhrt's criticism¹¹, the theory applies in certain regions, the labile region is not a region where it is applicable. Thus in the labile region the theory predicts more nuclei per sec. than there are molecules in the system!

In view of this it would appear that the Cahn-Hilliard theory¹² is a move in the right direction. The nucleus sizes in

table 8 also seem rather large, however it is probable that they may safely be taken as an indication of the relative sizes at the different supercoolings.

2. Effects of Stirring on Cell E.M.F.

The emf measurements of Benjamin and Strickland-Constable were always made on unstirred amalgams, the stirring being stopped for 30 sec. previous to measuring the emf when the amalgam was stirred. In the present experiments this procedure was found to be undesirable, since the emf of stirred cells was relatively steady, whereas the cell emf did not reach steady values for at least two minutes after the stirring was stopped. The effects of such interruptions of the stirring are shown in Figs. 24 and 25 for unsaturated and saturated amalgams respectively.

Unsaturated amalgams can be seen to reach steady values after about 2 - 3 min., whereas amalgams with excess zinc present required up to 10 min. to reach equilibrium. Stirring speed was found to affect the time required to reach steady values, as well as the magnitude of the overall emf change.

In practice, the emf recorded in most of the runs would have been less affected, since the emf was measured between two stirred electrodes. But, because the magnitude of the effects depended on whether excess zinc was present or not, and also because the stirred emfs were ~~not~~ quite reliable, the stirring was not interrupted in the present work.

Figure 25
EFFECT OF INTERRUPTING STIRRING

Saturated Electrode (large excess of Zn)

E.M.F. meas'd against Dilute, Unstirred Electrode

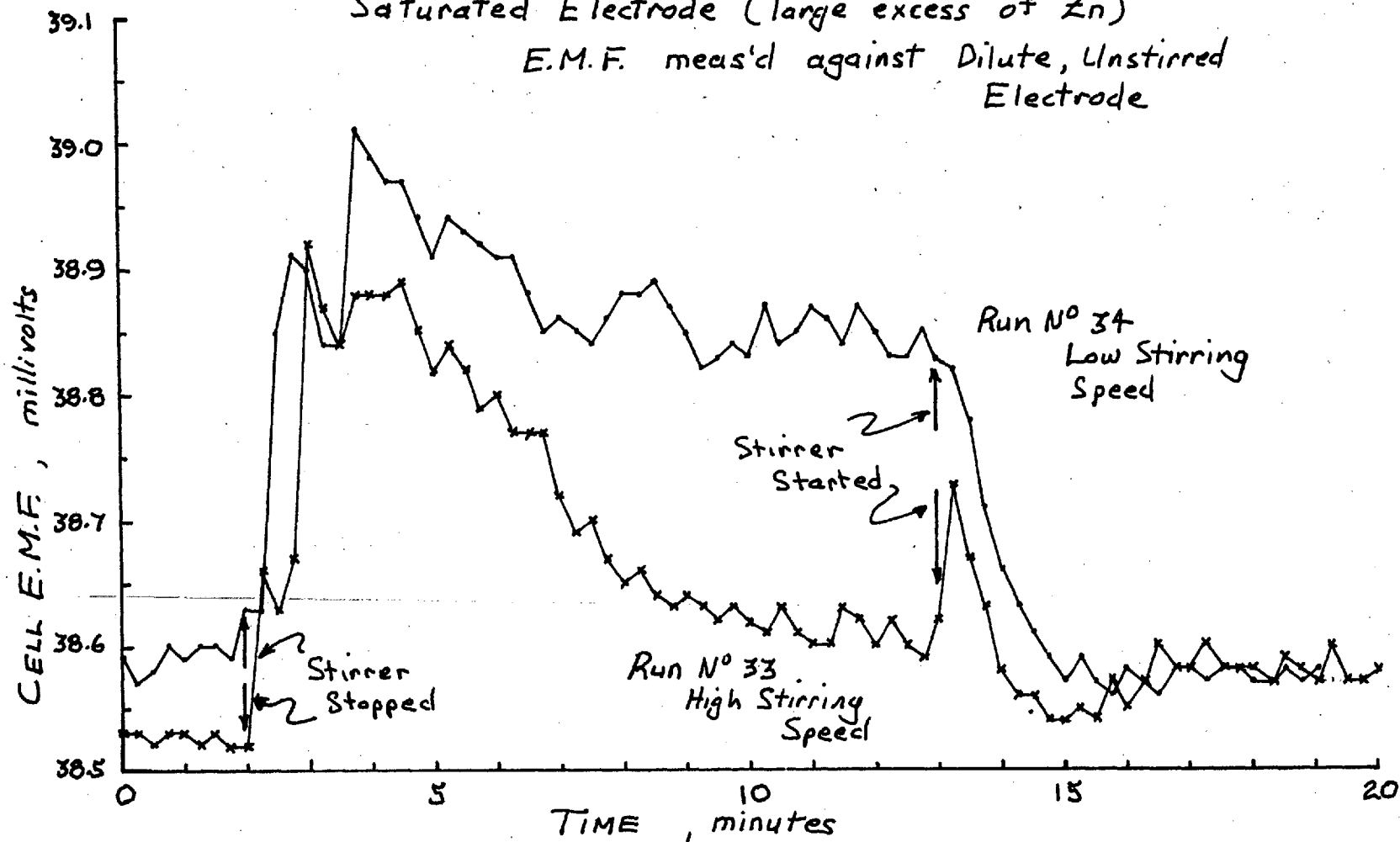


Figure 25
EFFECT OF INTERRUPTING STIRRING

Saturated Electrode (large excess of Zn)

E.M.F. meas'd against Dilute, Unstirred Electrode

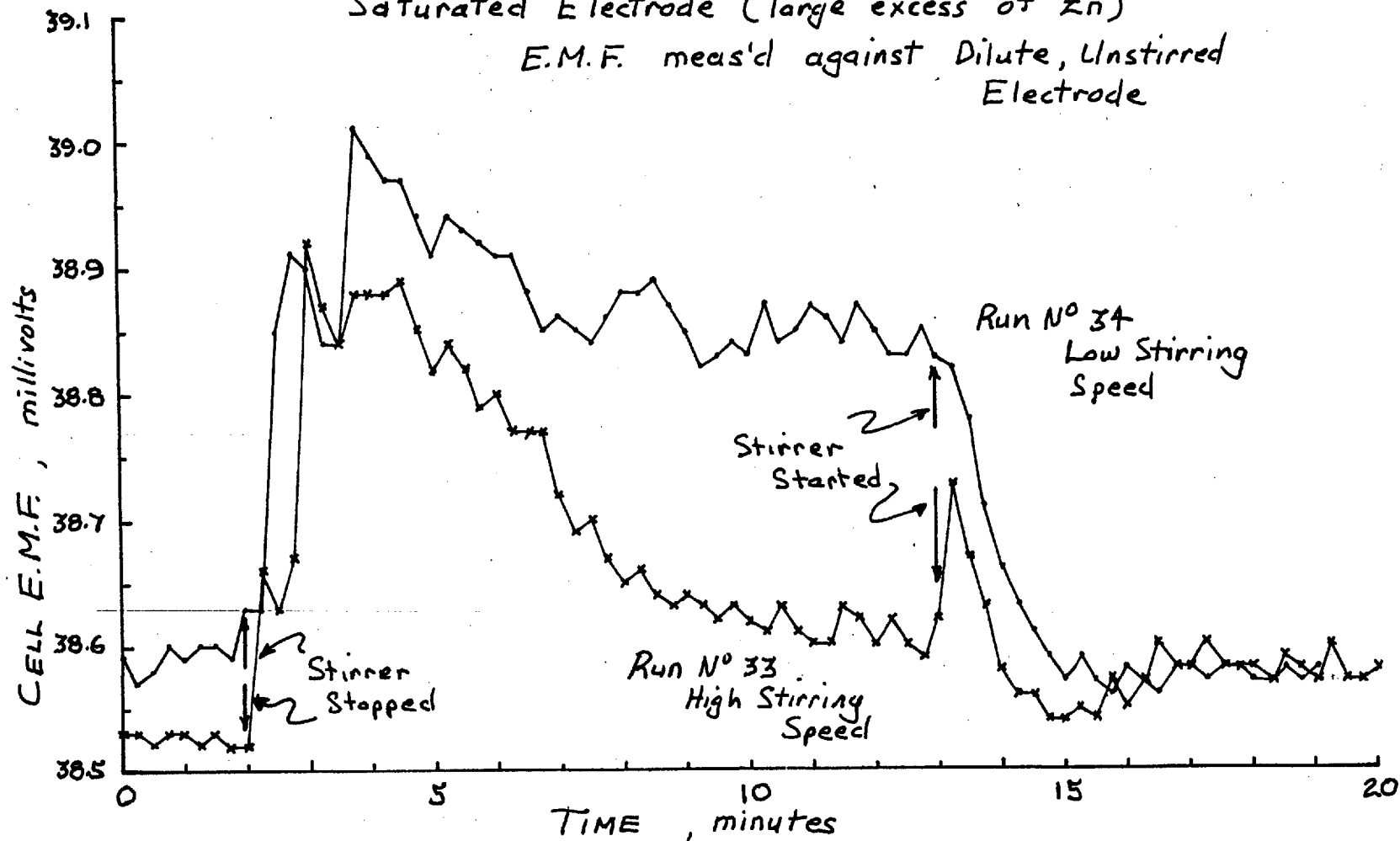


TABLE 9

SUMMARY OF INOCULATION RUNS, Zn - Hg SOLUTIONS

Run Number	T _s , °C	T _s , °C	Supercooling, ΔT, °C	Cooling Rate, C/hr.	Yield, grams/cc °C	Stirring Time, t, hrs.	Number of Crystals per c.c.					Remarks
							Above 3.0mm	2.0-2.9mm	1.0-1.9mm	0.5-0.9mm	Below 0.5mm	
155	34.9	21	0.5	2.4	0.026	8.1	0	0	0	0	2,800	free crystal
186	36.4	21	0.4	2.0	0.020	15	0	0.2	13.0	160	2,600	seed immersed 12 minutes
197	35.7	19.5	0.0	3.0	0.019	6.1	0	0	0	200	1,700	continuously cooled (see text)
203	27.0	22	0.0	0.3	0.021	15.3	0		27.3.....		260	continuously cooled
216	27.5	24-26	-0.1	0.25	0.019	21	0	0	4.1	8.3	4	continuously cooled
243	26.2	20.8	0.3	0.25	-	23.5	0	0	8.6	37.4	1,500	
258	27.5	23.5	0.0	0.25	0.023	19.8	0	0	13.6	48.2	175	
247	28.4	20.4	0.3	0.25	0.020	3	0.2	14.3	41.4	8.0	1,500	
271	27.4	25.3	0.3	0.125	0.021	0	3.1	2.4	0	0	0	not stirred
208	24.0	20.3	0.1	0.25	0.023	0	0	0	1.0	1.6	0	not stirred continuously cooled

Appendix II

Aqueous KBr Solutions

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| 12. Breeding of KBr Crystals. | p. 113 |

1. Determination of Solubility

The solubility data for aqueous KBr solutions available in the literature^{23,24} were found to be in considerable disagreement. Hence the solubilities at five degree intervals between 20°C - 50°C were determined. A 500 ml flask containing a solution with excess KBr was immersed in the water bath at each temperature (controlled within 0.05°C). The slurry was alternately violently agitated and allowed to settle over a 90 min. period, this being sufficient for equilibrium between the phases to be attained.

The determinations of KBr content in a weighed sample of clear solution were made in the order in table 10. Analysis by titration against standard AgNO_3 (using $\text{K}_2\text{Cr}_2\text{O}_7$ as indicator) and by evaporation to dryness gave essentially the same result.

Table 10 - SOLUBILITY OF KBr

Determination	T, °C	Wt. % KBr	
		(titration)	(evaporation)
1	20.4	39.75	39.95
2	50.0	44.76	44.68
3	40.0	43.34	43.59
4	30.0	41.72	
5	25.0	40.79	
6	35.0	42.58	
7	45.0	44.23	
8	50.0	44.95	

The results are plotted in Graph 26 and can be seen to agree fairly well with the most recent values available.

Figure 26
SOLUBILITY OF POTASSIUM BROMIDE
IN WATER

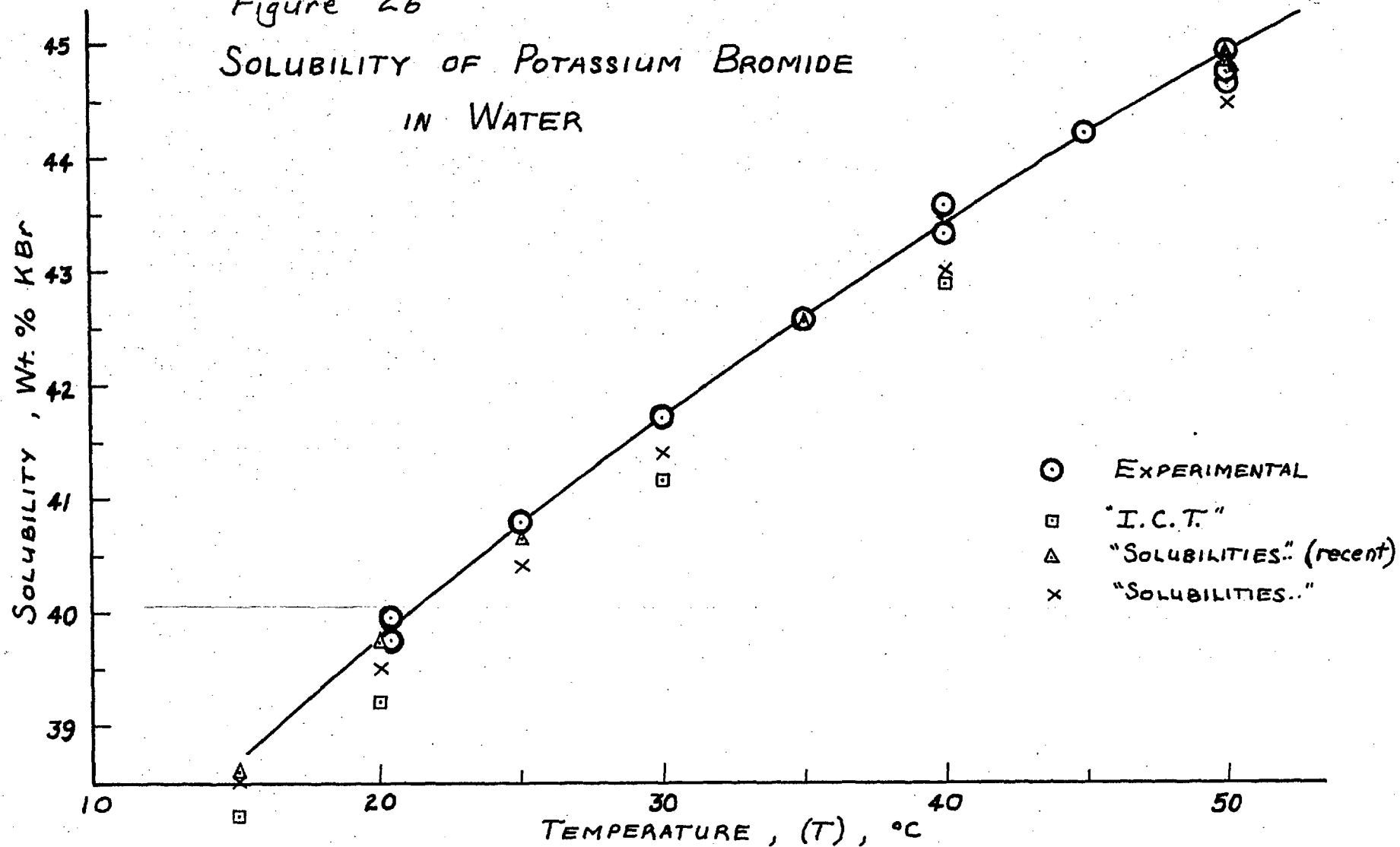


TABLE 11 Aqueous KBr Solutions at 32.5°C

U N S T I R R E D						S T I R R E D							
RUN NUMBER	SUPERCOOLING °C	SUPERSATURATION	GROWTH RATE (downward), cm/sec x 10 ⁶	GROWTH RATE (across), cm/sec x 10 ⁶	IMMERSION TIME minutes	SUPERCOOLING °C	SUPERSATURATION	STIRRING SPEED r.p.m.	CRYSTAL WIDTH cm	STIRRING TIME minutes	RELATIVE VELOCITY cm/sec	GROWTH RATE (downward), cm/sec x 10 ⁶	GROWTH RATE (across), cm/sec x 10 ⁶
Run	ΔT	S	dl/dt	dw/dt	t_1	ΔT	S	N	d_s	t_s	V	dl/dt	dw/dt
346	0.4	1.0014	3.3	1.5	75	0.3	1.0012	160	0.159	105	2.4	6.4	10.3
347	2.0	1.0083	42	30	90	1.1	1.0045	600	.300	15	15.0	117	86
348					10	1.9	1.0078	960	.156	20	12.5	212	159
350	3.9	1.0159	39	38	20	3.8	1.0154	160	.142	12	1.9	182	
351	3.9	1.0159	78	93	11	3.8	1.0152	425	.168	16	5.9	386	
352						4.1	1.0164	50	.136	32	0.6	158	
355	7.2	1.0289	190	175	10	6.3	1.0256	400	.284	6	9.5	648	
356	7.2	1.0289	135	131	12	6.2	1.0249	90	.312	7	2.3	205	
356						2.9	1.0119	160	.486	6	6.5	292	
357	7.1	1.0285	100	117	13	6.4	1.0259	850	.257	7	18.2	795	
359	7.2	1.0289	179	175	9	6.0	1.0242	50	.312	11	1.3	170	
361	6.2	1.0249	117	82	10	6.0	1.0240	50	.194	6	0.8	143	
361						5.1	1.0206	100	.298	5	2.5	167	
362	6.2	1.0249	129	93	10	5.6	1.0225	3000	.269	3	67.0	1005	
363	6.2	1.0249	152	131	10	5.1	1.0204	600	.343	3	17.1	1005	
364	6.8	1.0275	164	108	14			1000	.265		22.0		
365	6.8	1.0275	53	94	12	6.0	1.0242	5000	.125	3	51.9	815	
366	6.3	1.0254	161	137	10	5.6	1.0225	960	.265	5	21.1	645	
367	6.3	1.0254	155	136	10	5.4	1.0216	5000	.296	1	123	1490	

Figure 27
EFFECT OF SUPERSATURATION ON GROWTH RATE

KBr at 32.5°C - (100) faces
(unstirred)

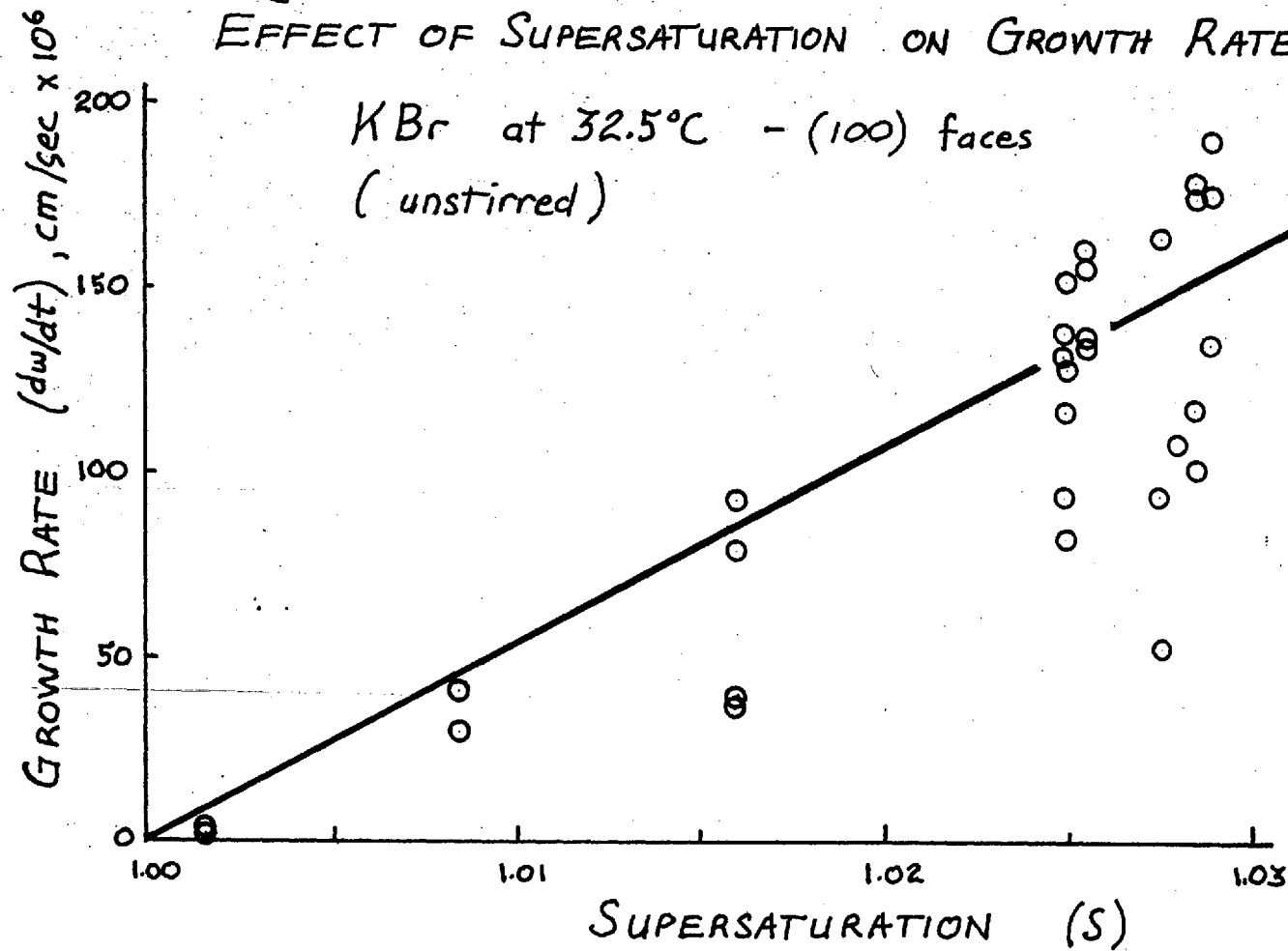


TABLE 12 BREEDING OF KBr CRYSTALS

RUN NUMBER	SUPERCOOLING °C	IMMERSION TIME Before Stirring, min.	STIRRING TIME min.	STIRRING SPEED rpm	RELATIVE VELOCITY cm/sec	STIRRED GROWTH RATE ⁶ (downward), cm/sec x 10 ⁶	CRYSTAL ADDED Wet(W) or Dry(D)	FINAL CRYSTAL Single(S) or Aggregate(A)	TRUE BREEDING	SPLINTERING OR OTHER CRYSTALS	REMARKS
Run	ΔT	t_I	t_s	N	V	dL/at	W/D	S/A	TB	Spl.	Remarks
360	6.2		20	1000	43.2		W		no	no	'Perspex' Model
346	0.3	75	105	160	2.4	6.4	D	A	no	no	no breeding
347	1.1	90	15	600	15.0	117	D	A	no	no	
348	1.9	10	20	960	12.5	212	W	A	yes	yes	Crystals fell on stirring, then shower fell
350	3.8	20	12	160	1.9	182	D	A	yes	yes	Same as above, smaller shower
351	3.8	11	16	425	5.9	386	D	S	yes	no	2 large bits fell, no shower
352	4.1	0	32	50	0.6	158	D	A	no	no	
355	6.3	10	6	400	9.5	648	W	S	yes	yes	Seed shattered on stirring - shower
356	6.2	12	7	90	2.3	205	D	S	no	no	
356	2.9		6	160	6.5	292	-	S	no	no	continuation of above run.
357	6.4	13	7	850	18.2	795	W	S	no	yes	Crystals came off support rod.
359	6.0	9	11	50	1.3	170	D	S	yes	yes	
361	6.0	10	6	50	0.8	143	W	S	no	no	
361	5.1		5	100	2.5	167	-	S	no	no	continuation of above run.
362	5.6	10	3	3000	67.0	1005	W	S	no	yes	about 5 crystals seen when V very high
363	5.1	10	3	600	17.1	1005	W	S	no	no	
364		14		1000	22.0		W	-	yes	yes	Seed fell on stirring - large shower
365	6.0	12	3	5000	51.9	815	W	A	no	yes	a few crystals seen at very high agitation
366	5.6	10	5	960	21.2	645	W	S	yes	yes	large chunks fell - slight shower
367	5.4	10	1	5000	123	1490	W	-	yes	yes	seed shattered on stirring - shower

TABLE 12 (concluded)

Run	ΔT	t_I	t_S	N	V	dI/dt	W/D	S/A	T.B.	Spl.	Remarks
413(a)	2.0	0	40	400	-	-	D	-	-	-	no growth
(b)	4.0	0	$\frac{1}{4}$	400	-	-	W	-	no	yes	Crystal broke, halves retained by glue - large shower (1000's)
(c)	4.0	0	5	400	-	-	D	-	no	no	No Breeding
(d)	4.0	6	$\frac{1}{4}$	400	-	-	D	A	yes	yes	Above Crystal re-introduced - Shower (2-300)
414(a)	4.0	10	10	400	-	-	D	A	no	no	
(b)	4.0	5	5	400	-	-	D	-	yes	no	very few small particles fell on stirring
(c)	4.0	5	$\frac{1}{2}$	400	-	-	D	A	yes	yes	Above Crystal re-introduced Shower (200)
415(a)	4.0	0	3	400	-	-	D	-	yes	yes	Shower (300)
(b)	4.0	0	1	400	-	-	D	A	yes	no	Above Crystal re-introduced - about 10 fell
416(a)	4.0	0	2	400	-	-	D	-	yes	yes	Small Shower (200)
(b)	4.0	0	2	400	-	-	W	-	yes	yes	Above Crystal re-introduced. Shower 100
(c)	6.0	0	1	400	-	-	W	S	yes	yes	Above Crystal re-introduced. Shower 100
417(a)	5.0	0	1	400	-	-	D	-	yes	yes	Shower 200
(b)	5.0	10	$\frac{1}{2}$	1000	-	-	-	-	yes	yes	Above Crystal re-introduced, broke Shower 1000's
418(a)	5.0	20	2	1000	-	-	-	S	yes	yes	About 50 crystals formed or broke off
(b)	5.0	-	-	1000	-	-	-	-	-	yes	Crystal touched to glass. Shower of 1000's

2. Investigation of Crystal Structure

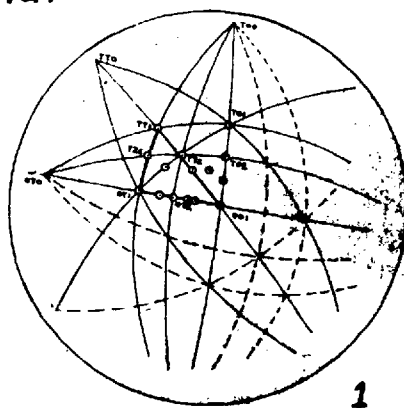
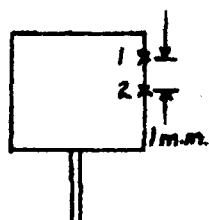
It was desired to determine with more certainty whether the relative degrees of internal ordering of the crystals in Figs. 13b and 13d corresponded closely with their appearance. A sample of each type of crystal was therefore mounted in an optical goniometer. The dis-ordered (aggregate) crystal gave only occasional reflections, which appeared to be random, while the single crystal of cubic outline showed a great many faces all reflecting at the one position. Only occasional reflections were obtained at other angles, and the cube faces were at 90° to each other.

X-ray diffraction photographs of the Laue (stationary back-reflection) type were taken of both crystals, and the stereographic projections obtained are shown in Fig. 28. Those of Fig. 28a represent two points at least one m.m. apart on the face of the cube of Fig. 13d. A comparison shows no detectable mismatching of faces of this separation, and a single crystal is indicated.

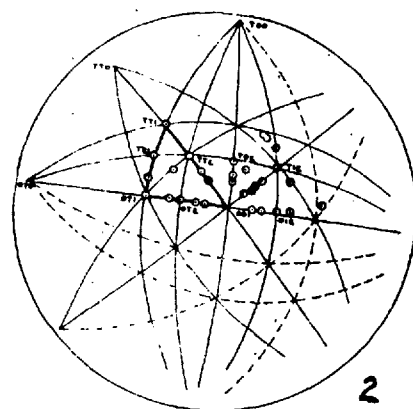
For the rounded crystal, Fig. 28b shows that a great deal of mis-matching was present, even for adjacent faces (projections 5a and 5b were obtained from one photograph). Projection 4 represents a photograph taken 1 m.m. from 5, and 8 was taken at 90° to both these. Table 13 below summarizes the angles between the $[101]$ planes, as measured from the projections, as well as the angles of translation required to bring the (111) poles into coincidence. The angles are relative to the 5a projection.

FIGURE 28 X-RAY DIFFRACTION STUDIES (KBr)

a) Single Crystal

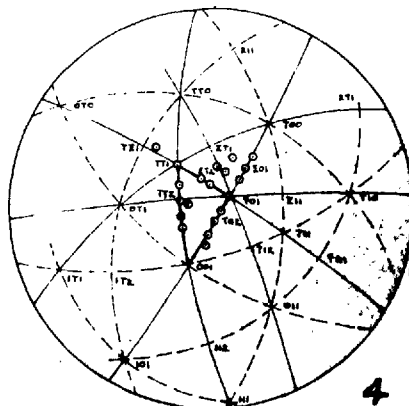
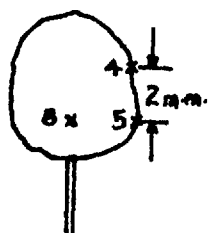


1

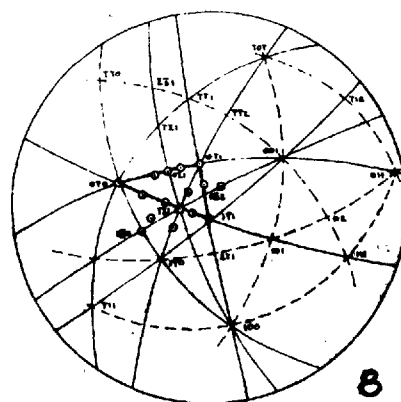


2

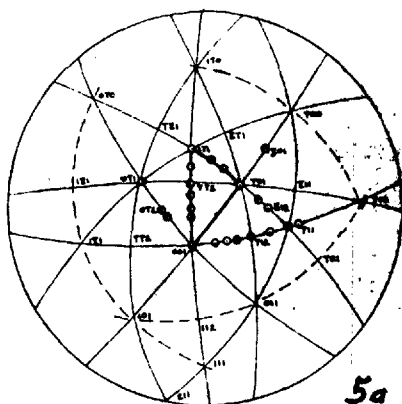
b) Aggregate



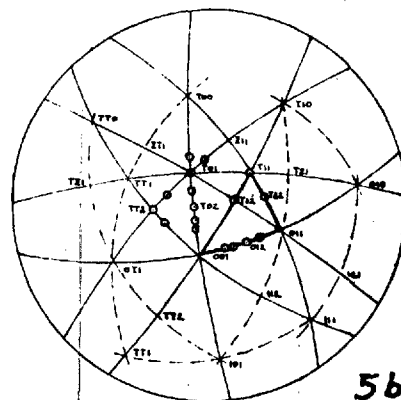
4



8



5a



5b

Table 13 - Mismatch in KBr Aggregate

Angle	Translation angle	Angle between 101
5a-5b	7°	41°
5a-4	10°	4°
5a-8	26°	28°

Since the maximum possible mismatch is 45° , these results indicate an almost random orientation of one crystal grain with the next. The maximum error in this analysis was of the order of 2° . The analysis shows that the structural mismatching of the crystals were well indicated by their appearance.

3. Growth of Whiskers on KBr Crystals

It was noted after some runs that, when the seed crystal was removed from a solution and wiped clean of excess solution (using damp cotton wool), whiskers soon appeared on the crystal surface. Fig. 29 shows photographs of such whiskers. Because they could be produced, though not in such large numbers, simply by wiping a dendritic crystal with a damp cloth and then leaving the crystal, it seems clear that a necessary condition for growth of these whiskers is an evaporating layer of liquid on the crystal surface; it is assumed that some special surface structural feature is also necessary.

The irregular surfaces of the whiskers and the above conditions suggest growth by a mechanism of capillary rise in a hollow crystal, as has been mentioned by Nabarro and Jackson³⁷. That the whiskers

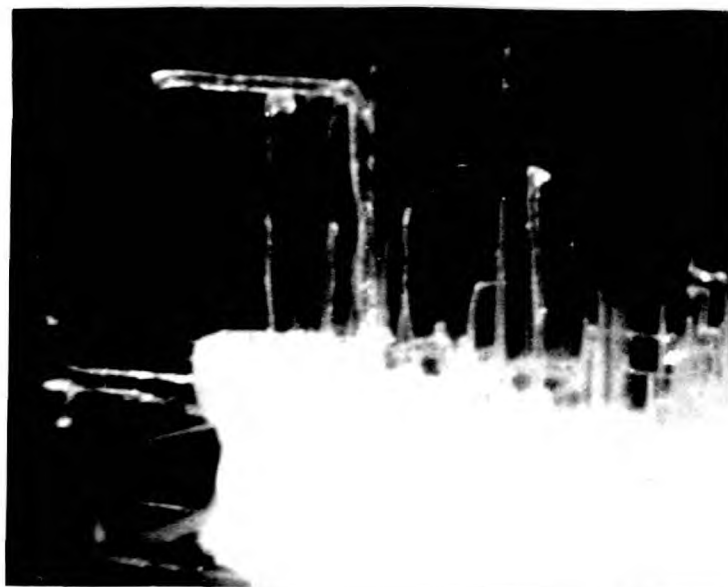
Figure 29 - WHISKERS ON KBr

(a)



x45

(b)



x135

are part of the lattice of the underlying crystal is suggested by their orientation normal to the crystal surface, and the occurrence of right angle bends.

Whiskers were never observed on the highly mis-oriented aggregate crystals.

Appendix III

Aqueous $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ Solutions

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TABLE 14

 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, stirred, 32.5°C

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RUN NUMBER	SUPERCOOLING, ($^\circ\text{C}$)	SUPERSATURATION (gms Hydrate/total gms)	STIRRER SPEED (rpm)	CRYSTAL WIDTH (cm)	CRYSTAL LENGTH (cm)	GROWTH RATE, $\frac{a}{a_0} \frac{d}{dt}$ cm/sec $\times 10^6$	GROWTH RATE, $\frac{a}{a_0} \frac{b}{b_0} \frac{d}{dt}$ cm/sec $\times 10^6$	CRYSTAL QUALITY (good, veil, hollow)	BREEDING TIME (min)
Run	ΔT	S	N	a	l	a_l/a_t	a_b/a_t	X1	t_1
309	3.9	1.0350	50	.177	.56	190	23	h	
309	4.0	1.0354	150	.095	.41	130	30	v	25
309	3.9	1.0352	300	.104	.41	127	33	g	
310	3.9	1.0348	50	.097	.54	41	16	g	
312	3.9	1.0350	150	.125	.51	42	21	g	
310	3.9	1.0345	300	.135	.66	47	25	g	
310	3.9	1.0347	1000	.117	.65	57	33	g	
311	10.4	1.0985	50	.140	.4	1940	70	h	
312	10.4	1.0987	150	.093	.4	2820	-	h	2
311	10.4	1.0985	300	.142	.4	2520	189	h	5
311	10.4	1.0985	1000	.125	.4	3020	146	h	3
313	6.6	1.0625	50	.118	.32	908	49	h	12
313	6.6	1.0627	150	.130	.34	1110	88	h	8
313	6.6	1.0627	300	.146	.31	1460	160	h	6
313	6.6	1.0627	1000	.156	.31	1382	125	h	8
314	8.4	1.0785	50	.158	.17	270	20	h	
314	8.4	1.0784	300	.167	.29	346	28	h	25
315	8.3	1.0781	50	.113	.34	(175) (328)	34	h	
315	8.3	1.0781	300	.136	.26	350	22	h	50
316	10.2	1.0979	50	.134	.64	1350	94	h	2
316	10.2	1.0981	300	.128	.5	2670	182	h	21
316	10.2	1.0981	1000	.117	.43	2000	197	h	13
316	10.2	1.0981	1000	.132	.5	3460	267	h	13
317	18.4	1.1760	50	.117	1.70	5600	-	h	1
317	18.5	1.7777	300	.091	.48	6810	333	h	1
318	8.6	1.0803	50	.110	.25	183	44	h	6
318	8.6	1.0803	190	.110	.30	596	78	h	2
318	8.6	1.0803	300	.093	.37	912	61	h	2
318	8.6	1.0801	1000	.122	.49	975	81	v	3
319	4.4	1.0400	50	.124	.35	55	21	g	
319	4.4	1.0400	150	.125	.37	100 (130)	33	v	20
319	4.4	1.0401	300	.126	.33	65	18	g	
319	4.4	1.0401	1000	.134	.25	120 (349)	34	v	9
320	6.9	1.0638	50	.108	.49	(160)	41	vh	6
320	6.9	1.0638	150	.151	.43	416 (466)	59	h	5
320	6.9	1.0638	300	.150	.56	(710)	34	h	10

TABLE 14 (continued)

Run	ΔT	S	N	d	l	dl/at	dw/at	Xl	t ₁
320	6.9	1.0638	1000	.137	.53	484	56	h	3
369	4.4	1.0400	40	.078	.24	27	14	g	
371	4.4	1.0400	100	.081	.41	80	28	v	
384	4.7	1.0427	100	.080	.25	70	34	g	
380	4.5	1.0402	160	.078	.18	89	33	g	
377	4.5	1.0402	240	.080	.32	85	37	g	
372	4.5	1.0402	540	.078	.25	115	34	v	22
379	4.5	1.0402	1110	.081	.14	-	36	g	
376	4.5	1.0402	1300	.089	.16	200	54	-	3
373	4.4	1.0400	1500	.082	.33	169	43	v	4
385	4.7	1.0427	2500	.078	.20	139	40	-	3
378	4.5	1.0402	3080	.078	.29	132	48	-	3
393	6.6	1.0613	42	.121	.48	456	33	h	
396	6.6	1.0608	100	.117	.61	666	35	h	12
388	6.6	1.0615	240	.117	.29	510	56	h	13
387	6.6	1.0615	600	.119	.24	362	42	h	14
397	6.6	1.0613	660	.117	.39	680	47	h	2 $\frac{1}{2}$
394	6.6	1.0613	1200	.119	.33	583	81	h	1
392	6.6	1.0615	1850	.119	.19	931	97	h	3
395	6.6	1.0613	2730	.117	.42	1131	136	h	1 $\frac{1}{4}$
389	6.6	1.0613	2920	.117	.44	655	133	h	2
410	8.4	1.0784	50	.080	.24	833	48	h	3
407	8.4	1.0784	105	.078	.27	774	67	h	3
403	8.4	1.0782	150	.078	.27	1280	29	h	
403	8.3	1.0775	280	.117	1.05	1280	85	h	2
399	8.4	1.0782	280	.080	.37	716	83	h	1
409	8.3	1.0776	500	.516	.43	1380	47	h	2
405	8.4	1.0782	840	.082	.20	995	91	h	1
406	8.4	1.0784	1110	.080	.13	1020	112	h	1
408	8.4	1.0782	1920	.028	.30	1210	139	h	3 $\frac{3}{4}$
411	8.4	1.0780	2730	.117	.34	1360	158	h	1 $\frac{1}{2}$
412	8.4	1.0784	2760	.080	.14	2280	170	h	1 $\frac{1}{4}$
401	8.4	1.0782	3460	.078	.24	1560	181	h	1 $\frac{1}{4}$
420	1.8	1.0140	4020	.046	.10	38	37	g	6
443	0.9	1.0082	240	.080	.23	38.4	15.0	g	
444	0.9	1.0082	1010	.097	.15	44.5	19.9	g	
445	0.9	1.0082	5060	.082	.19	45.7	15.1	g	
447	2.8	1.0263	240	.148	.29	56.4	22.2	g	
448	2.8	1.0263	1100	.173	.29	60.2	30.1	g	
449	2.8	1.0263	4400	.142	.31	86.5	30.1	g	
451	2.6	1.0238	240	.082	.29	46.3	18.9	g	
452	2.6	1.0238	1000	.097	.23	55.7	20.9	g	
453	2.6	1.0238	4000	.097	.35	70.5	28.9	g	
455	1.2	1.0116	160	.140	.40	10.2	4.3	g	
456	1.2	1.0116	625	.164	.46	16.3	4.2	g	
457	1.2	1.0116	1880	.191	.58	16.1	4.7	g	
459	3.6	1.0339	280	.153	.47	69.6	32.5	g	
460	3.6	1.0339	1150	.180	.69	98.5	31.5	g	
461	3.6	1.0339	6550	.218	.65	170	67.6	g	

TABLE 15 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, stirred, 20.0°C

Run	ΔT	S	N	d	l	dl/dt	dw/dt	Xl	t_1
321	12.7	1.1419	50	.078	.30	727	52	h	$1\frac{3}{4}$
321	12.7	1.1417	300	.073	.41	1430	106	h	$1\frac{1}{4}$
322	5.4	1.0605	50	.101	.30	30.3	9.6	g	
322	5.4	1.0605	150	.083	.36	40.7	13.5	g	
322	5.4	1.0605	300	.112	.44	43.2	7.2	g	60
322	5.4	1.0605	1000	.093	.37	50.4	13.3	g	
323	7.9	1.0882	50	.109	.36	161	18.3	h	16
323	7.9	1.0882	300	.098	.31	199	17.1	h	13
323	7.9	1.0882	1000	.078	.24	255	43	v	$1\frac{3}{4}$
325	7.5	1.0840	50	.080	.53	55	14.2	g	
325	7.4	1.0820	200	.179	.72	166	22.5	v	$1\frac{1}{2}$
325	7.5	1.0840	150	.105	.42	111	19.9	v	4
325	7.5	1.0840	300	.063	.41	88	14.6	v	11
325	7.5	1.0840	1000	.078	.33	112	16.5	v	19

TABLE 16 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, stirred, 45.0°C

Run	ΔT	S	N	d	l	dl/dt	dw/dt	Xl	t_1
326	10.1	1.0880	150	.109	.80	1170	124	-	$\frac{3}{4}$
327	6.1	1.0528	50	.093	.40	72	37	h	
327	6.1	1.0528	150	.129	.42	151	45	v	8
327	6.1	1.0528	300	.110	.31	424	52	h	6
327	6.1	1.0528	1000	.117	.26	545	80	h	5
328	7.7	1.0670	50	.120	.41	193	51	h	6
328	7.5	1.0653	150	.156	.58	1480	53	h	$1\frac{1}{2}$
328	7.7	1.0670	300	.102	.39	1490	50	-	2
328	7.7	1.0669	1000	.119	.37	1560	135	h	$1\frac{1}{4}$
329	4.6	1.0397	50	.101	.46	45	32	g	
329	4.8	1.0417	150	.142	.28	64	37	g	
329	4.8	1.0415	300	.165	.37	54	33	-	
329	4.8	1.0418	1000	.106	.28	112	48	g	39
330	1.5	1.0135	150	.255	.55	42	23	g	

TABLE 17

MgSO₄·7H₂O, unstirred, 32.5°C

RUN NUMBER	SUPERCOOLING, (°C)	SUPERSATURATION	CRYSTAL WIDTH (cm)	CRYSTAL LENGTH (cm)	GROWTH RATE, $c_{\text{dir}} \cdot n$ (cm/sec x 10 ⁶)	GROWTH RATE, $a_{\text{hdir}} \cdot n$ (cm/sec x 10 ⁶)	CRYSTAL QUALITY (good, veil, hollow)	GRASHOF NUMBER $(\frac{d^3 \rho^2 \eta g (s-1)}{\mu^2})$	SCHMIDT NUMBER $(\frac{\mu}{M D})$	SURFACE SUPERSAT'N	SUPERSAT'N ACROSS INTERFACE	MASS TRANS. COEFF. (gms/sec cm ²) x 10 ⁶	SPHEROID NUMBER (kg/d)
Run	ΔT	S	d	l	$\Delta l/\Delta t$	$\Delta w/\Delta t$	XL	Gr	Sc	S_i	ΔS	K_p	Sh
309	1.7	1.0162	.032	.45	7	2	g	1.70	2.43	1.0077	.0085	396	.018
309	3.7	1.0354	.099	.53	22	8	g	106	2.57	1.0141	.0213	632	.091
310	3.7	1.0351	.128	.31	13	6	v	226	2.57	1.0127	.0224	450	.084
311	10.3	1.0986	.078	.55	821	31	h	128	3.05	1.0246	.0740	703	.090
313	6.5	1.0626	.055	.3	442	25	h	30.4	2.77	1.0225	.0401	1045	.087
314	8.2	1.0787	.163	.3	83	19	v	970	2.90	1.0200	.0587	544	.138
315	6.4	1.0613	.068	-	40	12	-	56.6	2.76	1.0167	.0446	452	.047
316	10.1	1.0986	.113	-	806	33	h	382	3.03	1.0253	.0715	775	.144
317	18.5	1.1778	.099	.2	3680	41	h	410	4.10	1.0276	.1502	458	.093
318	8.4	1.0805	.080	-	83	20	v	114	2.91	1.0205	.0600	560	.071
319	4.2	1.0403	.091	-	22	9	v	92.9	2.60	1.0149	.0254	595	.079
319	4.2	1.0403	.100	.13	18	8	v	123	2.60	1.0141	.0262	513	.074
320	6.7	1.0642	.144	.33	71	15	v	300	2.78	1.0181	.0461	547	.119
320	6.7	1.0642	.117	.47	63	15	v	5.26	2.78	1.0181	.0461	547	.097
368	4.2	1.0401	.035	.62	22	11	g	2.41	2.60	1.0161	.0240	770	.039
370	4.2	1.0401	.027	.27	26	11	g	4.73	2.60	1.0161	.0240	770	.030
385	4.5	1.0427	.033	.14	25	9	g	62.2	2.62	1.0149	.0278	544	.026
386	6.4	1.0616	.070	.20	51	20	v	3.56	2.76	1.0205	.0401	837	.089
390	6.4	1.0616	.027	.32	58	25	v	14.4	2.76	1.0224	.0392	1070	.043
458	3.5	1.0339	.159	.32	20	8	g	368	2.56	1.0144	.0195	690	.152
396	6.4	1.0616	.043	.21	225	21	h	14.4	2.76	1.0209	.0405	871	.057
391	6.4	1.0616	.058	.22	47	14	v	35.4	2.76	1.0177	.0439	534	.047
398	8.2	1.0784	.035	.18	133	28	v	9.59	2.89	1.0236	.0548	859	.041
399	8.2	1.0784	.033	.27	107	21	v	8.05	2.89	1.0209	.0575	614	.032
400	8.2	1.0784	.047	.17	100	21	v	23.2	2.89	1.0209	.0575	614	.044
402	8.2	1.0784	.041	.09	101	38	v	15.4	2.89	1.0267	.0517	1238	.079
404	8.2	1.0784	.035	.11	91	22	v	9.59	2.89	1.0213	.0571	650	.036
409	8.2	1.0784	.058	.17	55	22	g	43.5	2.89	1.0213	.0571	650	.059
411	8.2	1.0784	.054	.16	55	19	v	35.2	2.89	1.0200	.0584	548	.046
419	1.5	1.0140	.033	.21	13	5	g	1.63	2.42	1.0118	.0022	3820	.176
421	1.9	1.0179	.036	.21	17	8	g	2.67	2.45	1.0142	.0037	3630	.183
422	2.8	1.0272	.029	.17	21	9	g	2.09	2.51	1.0149	.0123	1230	.051
423	4.7	1.0451	.027	.26	50	11	v	2.59	2.64	1.0161	.0290	637	.026

TABLE 17 (concluded)

Run	ΔT	S	d	l	dl/dt	dw/dt	Xl	Gr	Sc	S_i	ΔS	K_p	Sh
424	6.6	1.0630	.053	.25	103	18	v	27.4	2.77	1.0194	.0434	696	.056
425	8.3	1.0800	.086	.21	(207)	29	h	144	2.90	1.0239	.0561	869	.117
426	10.3	1.0986	.062	.25	(295)	31	h	73.5	3.05	1.0246	.0740	704	.072
427	12.1	1.1157	.056	.11	(1215)	48	h	53.6	3.20	1.0294	.0863	934	.069
428	14.9	1.1430	.058	.38	(705)	68	h	70.3	3.48	1.0337	.1093	1045	.110
429	19.5	1.1871	.097	.31	(1713)	90	h	403	4.29	1.0375	.1493	1012	.209
432	25.2	1.2418	.121	-	6500	119	h	938	5.46	1.0418	.2000	1000	.309
442	0.8	1.0082	.041	.13	8	3	g			1.0096			
446	2.7	1.0263	.080	.18	22	7	g	42.2	2.43	1.0135	.0128	920	.105
450	2.5	1.0238	.128	.27	11	3	g	157	2.42	1.0100	.0138	365	.067
454	1.2	1.0116	.144	.29	4	1.6	g	112	2.40	1.0066	.0050	537	.108

Figure 30
GROWTH & DISSOLUTION OF $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
(unstirred, at 32.5°C)

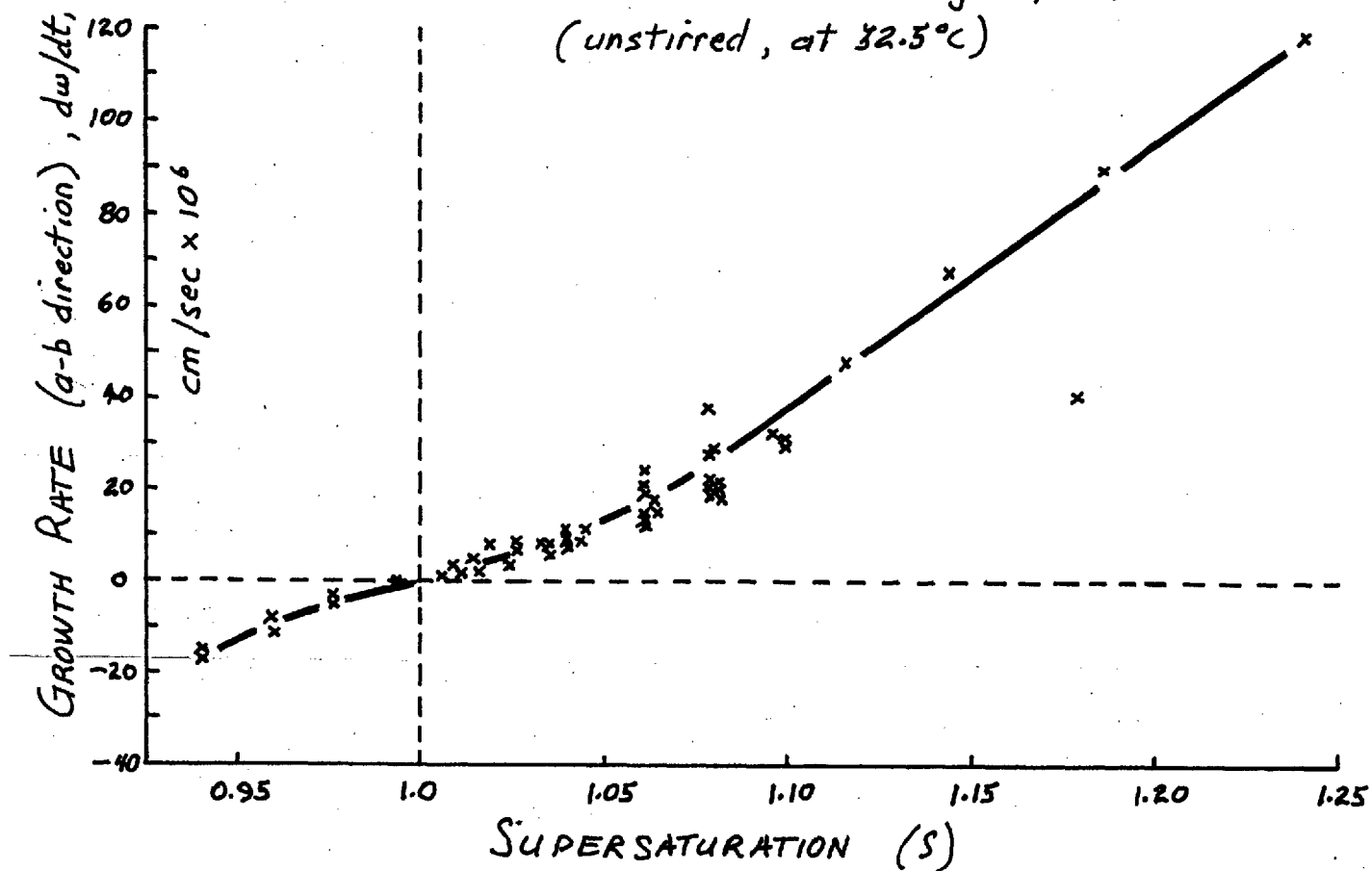


TABLE 18 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, unstirred, 20.0°C

Run	ΔT	S	d	l	dl/dt	dw/dt	XI	Gr	Sc	Sh	K_D	ΔS	S_i
221	12.7	1.1424	.058	.19	225	27	h	40.8	5.01	.079	695	.065	1.077
222	5.4	1.0606	.074	.24	16	5	v	42.8	3.98	.076	597	.014	1.060
223	7.9	1.0882	.080	.34	⁴⁶ (120)	15	v	74.5	4.30	.089	626	.039	1.051
224	29.2	1.326	.058	.40	5840	104	h	70.6	7.8	.102	527	.332	.994
225	7.5	1.0840	.058	.25	30	9	v	27.2	4.25	.069	676	.023	1.061

TABLE 19 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, unstirred, 45.0°C

Run	ΔT	S	d	l	dl/dt	dw/dt	XI	Gr	Sc	Sh	K_D	ΔS	S_i
326	10.1	1.0880	.081	.21	1070	54	h	207	2.15	.097	813	.111	.977
327	6.1	1.0528	.134	.24	36	13	v	440	1.94	.113	625	.034	1.019
328	7.7	1.0670	.082	.32	¹⁰⁹ (241)	34	h	169	2.02	.090	786	.073	.994
329	4.8	1.0420	.027	.34	32	16	g	3.94	1.88	.035	978	.027	1.015
330	1.5	1.0136	.062	.25	13	7.5	g	16.2	1.72	.048	622	.020	.993

TABLE 20 Horizontally Oriented Crystals (32.5°C)

Run	S	ΔT	N	d	l	dl/dt	dw/dt
308	1.0163	1.7	0	.027	.448	2.2	0.8
308	1.0163	1.7	300	.106	.715	33.7	7.8
332	1.0555	5.7	0	.074	.370	28.5	12.7
332	1.0536	5.6	50	.191	.785	104	19.2
332	1.0548	5.7	150	.129	.635	263	43.4
332	1.0554	5.7	300	.105	.474	240	42
332	1.0550	5.7	1000	.096	.600	337	58

TABLE 21 Dissolution of $MgSO_4 \cdot 7H_2O$ (32.5°C)

Run	ΔT	S	N	d	l	dl/dt	dw/dt
433	0.2	1.0060	0	.304	-	3.9	1.1
434	-0.2	.9915	0	.315	-	0	0
435	-2.4	.9766	0	.168	.42	-5.5	-4.3 (-2.8)
436	-4.1	.9602	0	.214	.39	-10.2	-8.1 (-11.3)
437	-6.0	.9416	0	.214	.28	-13.5	-14.8 (-16.2)
438	-6.0	.9416	2300	.307	1.05	-486	-117
439	-6.0	.9416	180	.245	.63	-197	-84
440	-6.0	.9416	680	.237	1.30	-920	-68
441	-6.0	.9416	3350	.206	1.10	-2040	-138

1. Growth Rates as a Function of Surface Supersaturation

Because the growth rates in the a-b directions have been used as a measure of the conditions at the crystal surface, it was desired to determine the absolute dependence of the growth rate on the surface supersaturation. Solutions were made up carefully at a number of different supercoolings, and a series of runs (442-461) at different stirring speeds carried out for each solution. With sufficiently high stirring speeds it was possible to eliminate the diffusional effects - a relative velocity of 106 cm./sec. was required at $\Delta T = 3.6^{\circ}\text{C}$.

When the growth rates were plotted against supercooling on a logarithmic scale, both the a-b and c direction rates were seen to be almost exactly 2.5 order. The equations determined for the growth rates, in cm./sec., at 32.5°C , were:

a-b ([100] , [010]) directions:

$$dw/dt = 0.326 (S_i - 1)^{2.5}$$

c ([001]) direction:

$$dl/dt = 0.841 (S_i - 1)^{2.5}$$

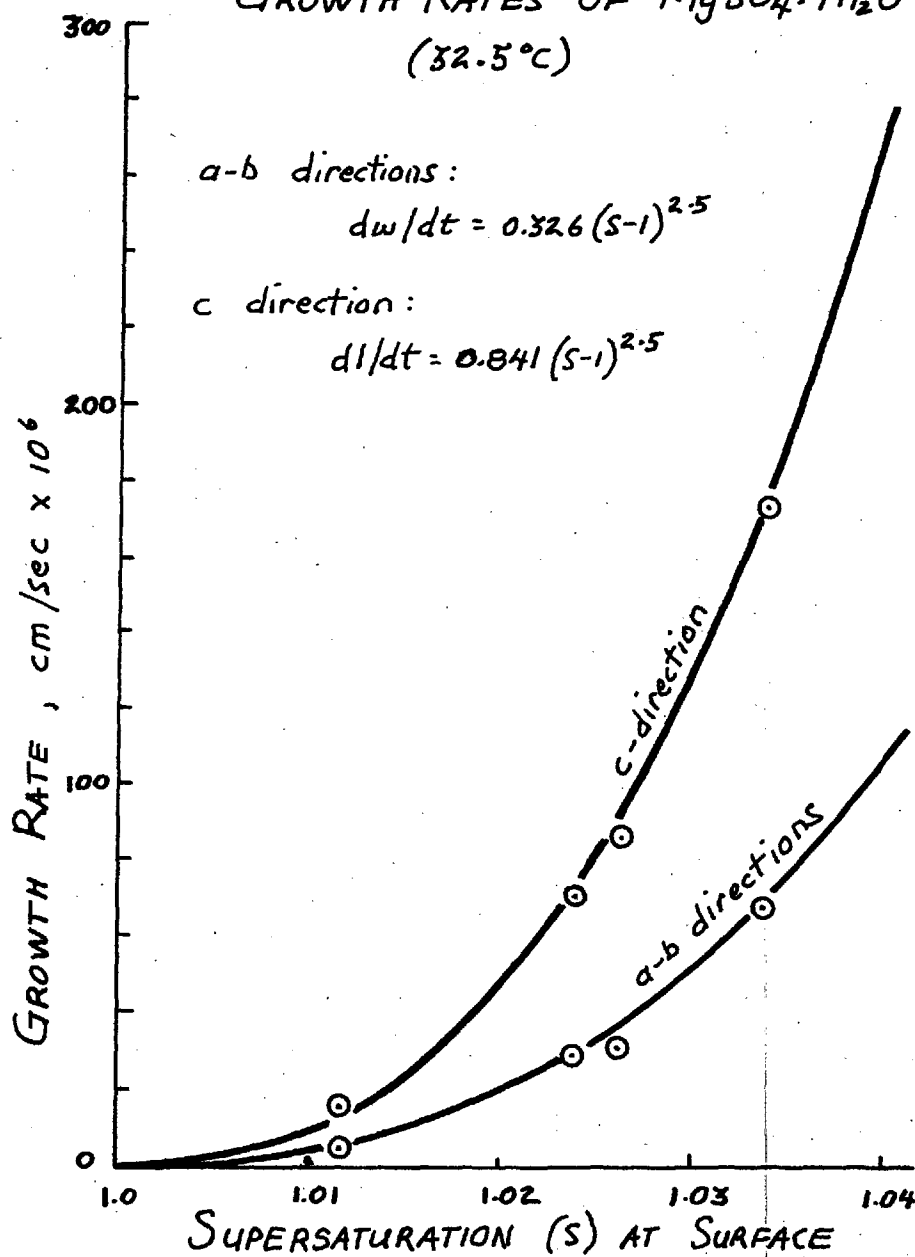
Thus the ratio of the rates in these directions is seen to be

$$\frac{dl/dt}{dw/dt} = \frac{0.841}{0.326} = 2.6$$

independent of the surface supersaturation. When diffusion is a factor smaller ratios would be expected - see equation (7).

Figure 31

GROWTH RATES OF $MgSO_4 \cdot 7H_2O$
(32.5°C)



It should be noted that these results do not agree with those of Hixon and Knox, who found a first order surface reaction.

2. Diffusion Correlations

The dimensionless correlation employed by Hixon and Knox has been applied here in the case of the individual linear growth rates, rather than the overall mass rates. The surface supersaturations were estimated from the equation

$$dw/dt = 0.361 (S_i - 1)^{2.5}$$

and these were then used to estimate the mass transfer coefficient in equation (5) and hence the Sherwood Number. The calculations are given in table 22.

An analysis of variance technique applied to 74 stirred results at 32.5°C indicates, for the a-b direction, that

$$Sh = 0.86 (Re)^{0.37 \pm 0.11} (Sc)^{-1.1 \pm 1.6},$$

the limits being for 95% confidence. The corresponding result for the c direction, based on 14 runs in which unflawed growth occurred, was

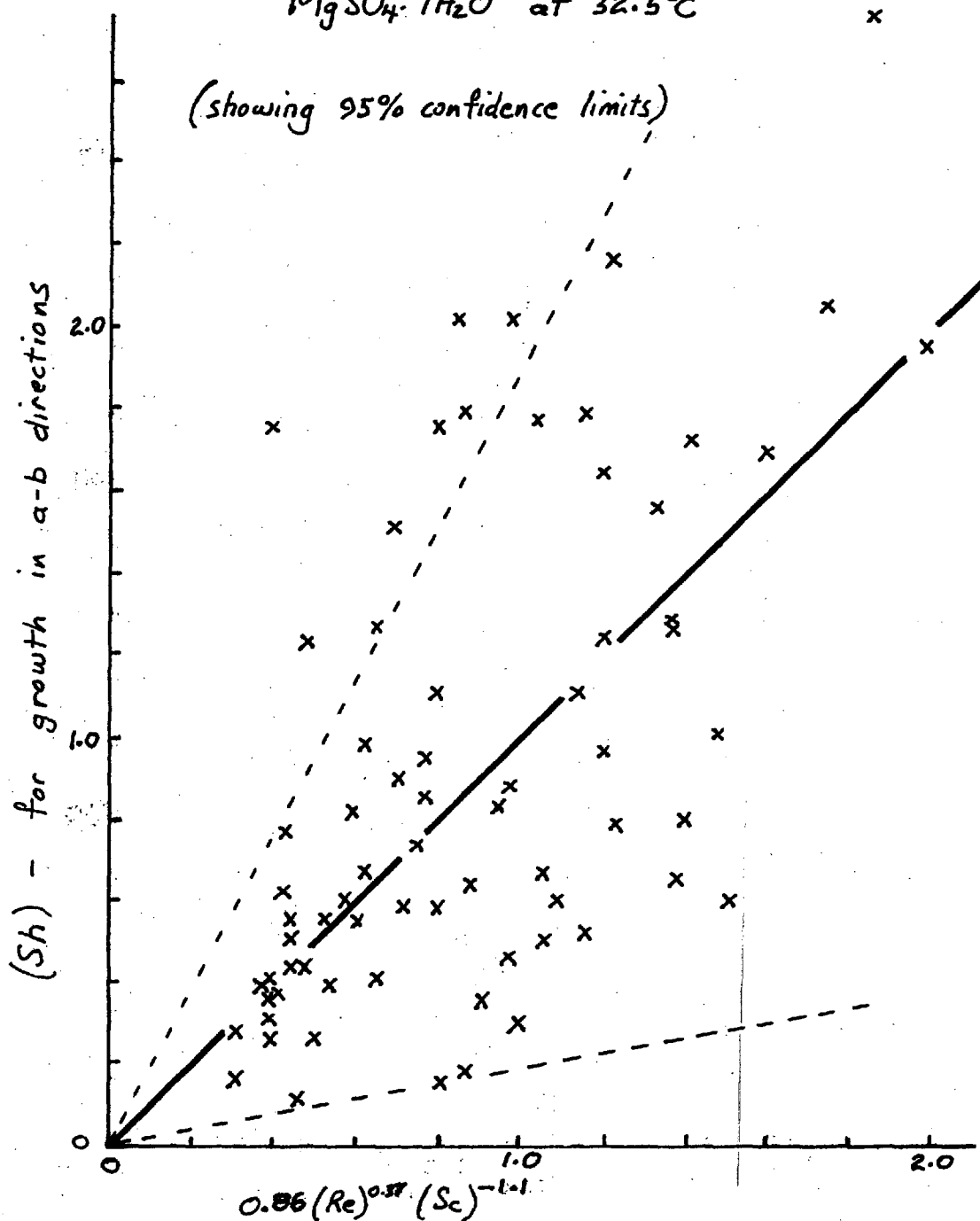
$$Sh = 2.0 (Re)^{0.50 \pm 0.20} (Sc)^{1.6 \pm 1.3}$$

Because of the wide confidence limits the results in the two directions are not mutually exclusive: it would be expected that they be the same. The limits also include the results of Hixon and Knox.

Figure 32
CORRELATION OF STIRRED RUNS

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ at 32.5°C

(showing 95% confidence limits)



The convection correlation for unstirred solutions given by Hixon and Knox has been applied to the unstirred runs at 32.5°C. The calculations are given in table 17, and the results are shown in Fig. 33, which indicates that

$$(\text{Sh}) = 0.021 (\text{Gr. Sc})^{\frac{1}{4}}$$

Figure 33

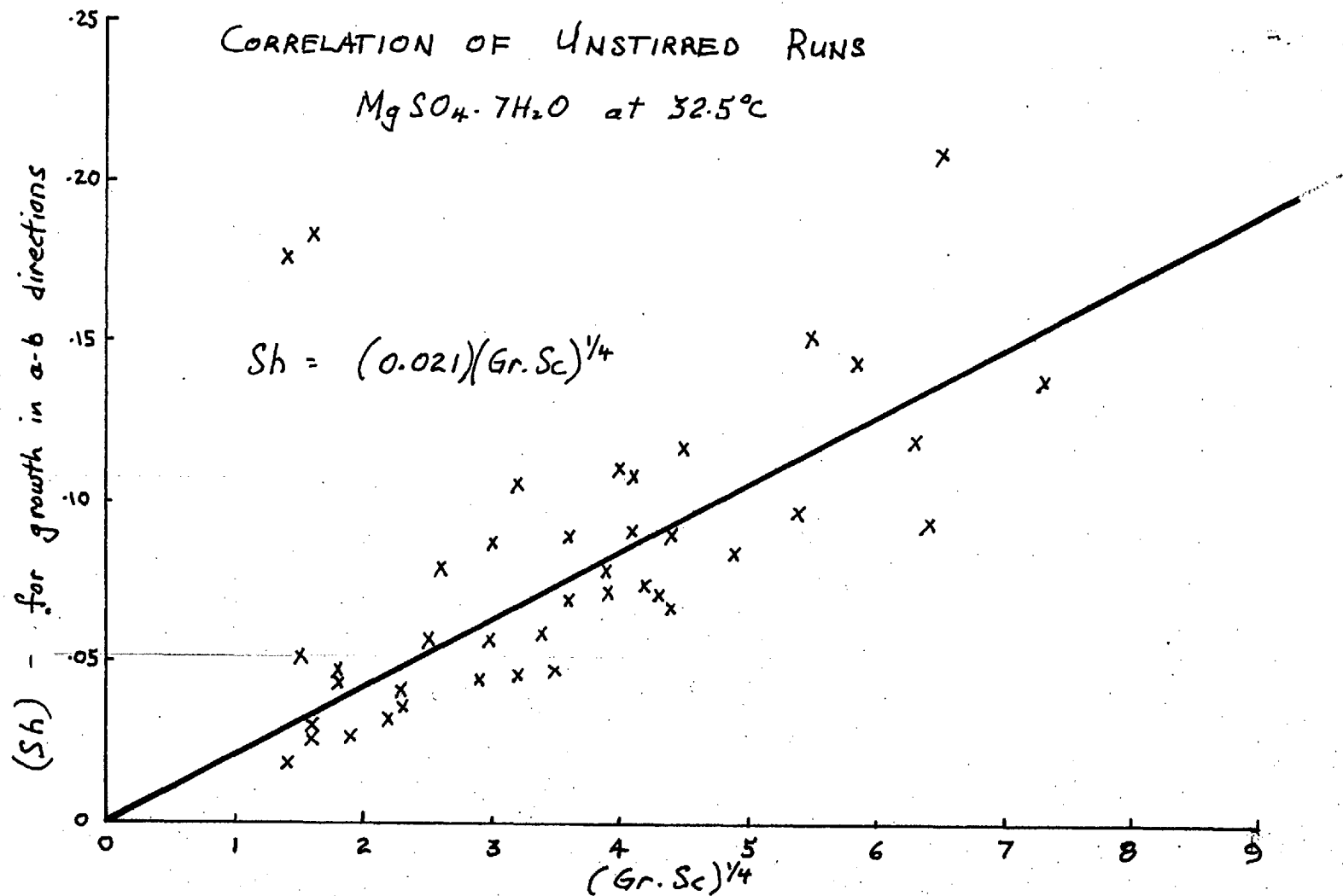


TABLE 22 Calculations Runs at 32.5°C

RUN NUMBER	RELATIVE VELOCITY cm./sec.	REYNOLD'S N° ($\frac{dV\rho}{\mu}$)	SCHMIDT N° ($\frac{\mu}{M D}$)	SURFACE SUPERSAT'N (wt. Basis)	SUPERSAT'N ACROSS INTERFACE	MASS TRANS. COEFF. (gms/cm ² sec) $\times 10^6$	SHERWOOD N° (Kd/D)
Run	V	Re	Sc	S ₁	ΔS	K _D	Sh
309	.66	3.68	2.57	1.0217	.0133	2900	.75
309	1.05	3.17	2.57	1.0243	.0111	4540	.63
309	2.31	7.62	2.57	1.0253	.0099	5610	.85
310	.36	1.11	2.57	1.0187	.0161	1675	.24
312	1.39	5.50	2.57	1.0209	.0141	2500	.45
310	3.00	12.83	2.57	1.0224	.0121	3470	.68
310	8.67	32.2	2.57	1.0253	.0094	5900	1.00
311	.52	2.16	3.05	1.0341	.0644	1830	.42
312	1.03	2.86	3.05	-	-	-	-
311	3.16	13.38	3.05	1.0505	.0480	6600	1.53
311	9.26	34.6	3.05	1.0452	.0533	4600	.94
313	.44	1.59	2.77	1.0297	.0318	2590	.47
313	1.44	5.77	2.77	1.0372	.0255	5800	1.15
313	3.24	14.57	2.77	1.0470	.0157	17100	3.80
313	11.56	55.5	2.77	1.0425	.0202	10400	2.46
314	.59	2.81	2.96	1.0205	.0580	579	.20
314	3.71	18.9	2.96	1.0236	.0548	856	.22
315	.42	1.44	2.96	1.0256	.0525	1090	.20
315	3.02	12.5	2.96	1.0215	.0566	653	.14
316	.50	1.98	3.04	1.0382	.0597	2650	.58
316	2.84	10.85	3.04	1.0498	.0483	6340	1.32
316	8.67	30.2	3.04	1.0513	.0468	7060	1.35
316	9.78	38.4	3.04	1.0580	.0401	11200	2.42
317	.43	1.41	4.05	-	-	-	-
317	2.02	5.12	4.09	1.0634	.1143	4900	.91
318	.41	1.36	2.91	1.0284	.0519	1425	.27
318	1.55	5.17	2.91	1.0355	.0448	2950	.51
318	2.07	5.83	2.91	1.0323	.0480	2130	.31
318	9.04	33.4	2.91	1.0361	.0440	3100	.59
319	.46	1.79	2.60	1.0209	.0191	1850	.34
319	1.39	5.48	2.60	1.0253	.0147	3780	.69
319	2.80	11.1	2.60	1.0196	.0205	1480	.28
319	9.90	41.8	2.60	1.0256	.0145	3950	.77
320	.40	1.33	2.78	1.0276	.0362	1900	.31
320	1.68	7.82	2.78	1.0319	.0319	3100	.72
320	3.33	15.4	2.78	1.0256	.0380	1490	.35
320	9.92	41.8	2.78	1.0313	.0325	2890	.61
369	.23	.57	2.60	1.0177	.0223	1050	.12
371	.60	1.53	2.60	1.0236	.0164	2870	.34

TABLE 22 (continued)

Run	V	Re	Sc	S _i	As	K _d	Sh
384	.59	1.49	2.62	1.0256	.0171	3340	.39
380	.93	2.27	2.60	1.0253	.0149	3720	.42
377	1.42	3.58	2.60	1.0265	.0137	4540	.53
372	3.12	7.68	2.60	1.0256	.0146	3920	.45
379	6.59	16.8	2.60	1.0262	.0140	4320	.51
376	8.57	24.0	2.60	1.0309	.0093	9750	1.26
373	9.10	23.5	2.60	1.0282	.0118	6120	.74
385	14.42	35.5	2.62	1.0274	.0153	4400	.50
378	17.30	43.8	2.60	1.0294	.0198	4080	.46
393	.38	1.41	2.78	1.0253	.0360	1540	.29
396	.87	3.14	2.76	1.0259	.0349	1690	.30
388	2.08	7.53	2.78	1.0313	.0302	3110	.56
387	5.28	19.4	2.78	1.0279	.0336	2100	.38
397	8.72	20.7	2.78	1.0304	.0309	2560	.46
394	10.57	38.9	2.78	1.0361	.0252	5400	.98
392	16.29	59.9	2.78	1.0387	.0228	7150	1.29
395	23.61	85.5	2.78	1.0439	.0174	13100	2.33
389	25.28	91.5	2.78	1.0435	.0178	12600	2.26
410	.30	.72	2.89	1.0249	.0490	1640	.21
407	.61	1.43	2.89	1.0335	.0449	2510	.31
403	.87	2.05	2.89	1.0239	.0543	900	.11
403	2.42	8.59	2.88	1.0367	.0408	3500	.64
399	1.66	4.04	2.89	1.0363	.0419	3330	.42
409	5.78	27.4	2.88	1.0292	.0484	1630	.40
405	5.10	12.7	2.89	1.0377	.0405	3780	.48
406	6.57	15.9	2.89	1.0408	.0376	5130	.64
408	11.09	26.2	2.89	1.0443	.0335	6900	.84
411	23.64	83.9	2.89	1.0467	.0313	8480	1.56
412	16.33	39.6	2.89	1.0483	.0301	9480	1.19
401	19.98	47.2	2.89	1.0497	.0285	10670	1.31
420	13.70	20.3	2.42	1.0265	-.0125	-	-
443	1.42	3.69	2.38	1.0182	-.0100	-	-
444	7.25	22.9	2.38	1.0204	-.0122	-	-
445	30.68	81.8	2.38	1.0182	-.0100	-	-
447	2.63	12.4	2.51	1.0212	.0054	6910	1.47
448	14.07	77.5	2.51	1.0243	.0020	-	-
449	46.25	209	2.51	1.0243	.0020	-	-
451	1.46	3.83	2.49	1.0200	.0038	8350	.98
452	7.18	22.3	2.49	1.0209	.0029	12100	1.67
453	28.72	89.1	2.49	1.0239	-.0001	-	-
455	1.66	7.54	2.40	1.0110	.0006	12050	2.35
456	7.57	40.2	2.40	1.0110	.0006	11800	2.69
457	26.59	165	2.40	1.0114	.0002	-	-
459	3.17	15.4	2.56	1.0250	.0089	6140	1.36
460	15.32	87.5	2.56	1.0248	.0091	5750	1.50
461	105.6	730	2.56	1.0336	.0003	-	-

Table of Symbols

A	Surface Area
B	Constant (Frequency factor)
C	Concentration
D	Diffusivity
d	Crystal width
E	e.m.f.
G	Gibb's function of activation
g	acceleration due to gravity
ΔG	Free energy of nucleus formation
Δg	Activation energy for self diffusion
h	Planck's constant
ΔH	Latent heat of fusion
I	Nucleation rate (nuclei / sec.)
k	Gas constant / molecule
K_D	Mass transfer coefficient
K_R	Surface reaction rate constant
l	Length
$\bar{M}$	Average molecular weight
m	Weight

N	No. of molecules / c.c. of solution
n^*	No. of molecules, surface of critical nucleus
r^*	Radius of critical nucleus
S	Supersaturation (bulk) $= \left(\frac{\text{mass fraction crystallizing component}}{\text{solubility mass fraction crystallizing component}} \right)$
S_i	Supersaturation at Crystal surface
T	Absolute temperature
T_s	Saturation temperature
ΔT	Supercooling
t	Time
V	Relative velocity between crystal and solution
V_m	Molar volume
γ	Activity coefficient
μ	Viscosity
ρ	density

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TABLE 9

SUMMARY OF INOCULATION RUNS, Zn - Hg SOLUTIONS

(Extra Copy)

Run Number	T _s , °C	T _s , °C	Supercooling, T, °C	Cooling Rate, C/hr.	Yield, grams/cc °C	Stirring Time, t, hrs.	Number of Crystals per c.c.					Remarks
							Above 3.0mm	2.0-2.9mm	1.0-1.9mm	0.5-0.9mm	Below 0.5mm	
155	34.9	21	0.5	2.4	0.026	8.1	0	0	0	0	2,800	free crystal
186	36.4	21	0.4	2.0	0.020	15	0	0.2	13.0	160	2,600	seed immersed 12 minutes
197	35.7	19.5	0.0	3.0	0.019	6.1	0	0	0	200	1,700	continuously cooled (see text)
203	27.0	22	0.0	0.3	0.021	15.3	0		27.3.....		260	continuously cooled
216	27.5	24-26	-0.1	0.25	0.019	21	0	0	4.1	8.3	4	continuously cooled
243	26.2	20.8	0.3	0.25	-	23.5	0	0	8.6	37.4	1,500	
258	27.5	23.5	0.0	0.25	0.023	19.8	0	0	13.6	48.2	175	
247	28.4	20.4	0.3	0.25	0.020	3	0.2	14.3	41.4	8.0	1,500	
271	27.4	25.3	0.3	0.125	0.021	0	3.1	2.4	0	0	0	not stirred
208	24.0	20.3	0.1	0.25	0.023	0	0	0	1.0	1.6	0	not stirred continuously cooled

TABLE 12 BREEDING OF KBr CRYSTALS

(Extra Copy)

RUN NUMBER	SUPERCooling °C	IMMERSION TIME Before Stirring, min.	STIRRING TIME min.	STIRRING SPEED rpm	RELATIVE VELOCITY cm/sec	STIRRED GROWTH RATE ⁶ (downward), cm/sec x 10 ⁶	CRYSTAL ADDED Wet(W) or Dry (D)	FINAL CRYSTAL Single(S) or Aggregate(A)	TRUE BREEDING	SPLINTERING OR OTHER CRYSTALS	REMARKS
Run	T	t _I	t _s	N	V	dI/dt	W/D	S/A	TB	Spl.	Remarks
360	6.2		20	1000	43.2		W		no	no	'Perspex' Model
346	0.3	75	105	160	2.4	6.4	D	A	no	no	no breeding
347	1.1	90	15	600	15.0	117	D	A	no	no	
348	1.9	10	20	960	12.5	212	W	A	yes	yes	Crystals fell on stirring, then shower fell
350	3.8	20	12	160	1.9	182	D	A	yes	yes	Same as above, smaller shower
351	3.8	11	16	425	5.9	386	D	S	yes	no	2 large bits fell, no shower
352	4.1	0	32	50	0.6	158	D	A	no	no	
355	6.3	10	6	400	9.5	648	W	S	yes	yes	Seed shattered on stirring - shower
356	6.2	12	7	90	2.3	205	D	S	no	no	
356	2.9		6	160	6.5	292	-	S	no	no	continuation of above run.
357	6.4	13	7	850	18.2	795	W	S	no	yes	Crystals came off support rod.
359	6.0	9	11	50	1.3	170	D	S	yes	yes	
361	6.0	10	6	50	0.8	143	W	S	no	no	
361	5.1		5	100	2.5	167	-	S	no	no	continuation of above run.
362	5.6	10	3	3000	67.0	1005	W	S	no	yes	about 5 crystals seen when V very high
363	5.1	10	3	600	17.1	1005	W	S	no	no	
364		14		1000	22.0		W	-	yes	yes	Seed fell on stirring - large shower
365	6.0	12	3	5000	51.9	815	W	A	no	yes	a few crystals seen at very high agitation
366	5.6	10	5	960	21.1	645	W	S	yes	yes	large chunks fell - slight shower
367	5.4	10	1	5000	123	1490	W	-	yes	yes	seed shattered on stirring - shower

TABLE 12 (concluded)

(Extra Copy)

Run	T	t_I	t_S	N	V	dI/dt	W/D	S/A	T.B.	Spl.	Remarks
413(a)	2.0	0	40	400	-	-	D	-	-	-	no growth
(b)	4.0	0	$\frac{1}{4}$	400	-	-	W	-	no	yes	Crystal broke, halves retained by glue - large shower (1000's)
(c)	4.0	0	5	400	-	-	D	-	no	no	No Breeding
(d)	4.0	6	$\frac{1}{4}$	400	-	-	D	A	yes	yes	Above Crystal re-introduced - Shower (2-300)
414(a)	4.0	10	10	400	-	-	D	A	no	no	
(b)	4.0	5	5	400	-	-	D	-	yes	no	very few small particles fell on stirring
(c)	4.0	5	$\frac{1}{2}$	400	-	-	D	A	yes	yes	Above Crystal re-introduced Shower (200)
415(a)	4.0	0	3	400	-	-	D	-	yes	yes	Shower (300)
(b)	4.0	0	1	400	-	-	D	A	yes	no	Above Crystal re-introduced - about 10 fell
416(a)	4.0	0	2	400	-	-	D	-	yes	yes	Small Shower (200)
(b)	4.0	0	2	400	-	-	W	-	yes	yes	Above Crystal re-introduced. Shower 100
(c)	6.0	0	1	400	-	-	W	S	yes	yes	Above Crystal re-introduced. Shower 100
417(a)	5.0	0	1	400	-	-	D	-	yes	yes	Shower 200
(b)	5.0	10	$\frac{1}{2}$	1000	-	-	-	-	yes	yes	Above Crystal re-introduced, broke Shower 1000's
418(a)	5.0	20	2	1000	-	-	-	S	yes	yes	About 50 crystals formed or broke off
(b)	5.0	-	-	1000	-	-	-	-	-	yes	Crystal touched to glass. Shower of 1000's