

AN INVESTIGATION OF SOME METHODS OF CHEMICAL PRECIPITATION IN THE ARTIFICIAL GROWTH OF CALCITE

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AN INVESTIGATION OF SOME METHODS OF CHEMICAL PRECIPITATION IN THE ARTIFICIAL GROWTH

OF CALCITE

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Robert F. Curren

A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

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By

Robert F. Curren

INTRODUCT ION

Many diverse forms of apparatus have been designed for the artificial growth of crystals, and a variety of chemical and physical principles are employed to this end. The underlying principle, common to all methods of growing crystals from solution, is that of producing a supersaturated solution (one containing an amount of the solute in excess of its normal solubility) from which ions may be deposited to build up the crystal lattice of a nucleus or seed crystal. In instances where seed crystals are introduced into such a solution it is desirable to keep the number of crystal nuclei which will form spontaneously at a minimum so that the growth will occur primarily upon the seed crystals. It is also desirable to keep the number of nuclei formed as small as possible when crystals are to be grown without seeding the solution so that the crystals thus formed will reach the maximum possible size.

The number of crystal nuclei which will form depends upon the degree of supersaturation of the solution as expressed by the Von Weimarn ratio Degree of supersaturation = $\frac{Q-L}{L}$

where Q is the total concentration of the salt in solution and L is the equilibrium solubility of the salt. It is apparent from the above relationship that the most favorable conditions for crystal growth are obtained when a state of continuous but slight supersaturation exists in the solution from which the crystals are to be grown.

This condition may be readily obtained when the material to be grown has a reasonably high solubility by evaporating at a slow rate a portion of the solvent from a saturated solution of the salt. When provision is made to prevent the formation of additional crystals at the surface of the solution and to provide for adequate circulation of the solution around the suspended seed crystal, this method produces excellent results and has been used successfully to produce crystals of a considerable number of substances.

Advantage is taken of the appreciable difference in solubility with temperature which is a property common to a number of substances. By changing the temperature of a saturated solution slowly in the direction of decreasing solubility, a condition of supersaturation is obtained in the solution and growth upon the crystal occurs. The actual apparatus employed generally provides some means whereby the solution is heated at one point in the presence of an excess of the salt and conducted to the point at which the crystal is suspended, where it is cooled to decrease the solubility of the salt. Naturally, in substances whose solubility decreases with increasing temperature the heating and cooling processes are interchanged.

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Frequently less direct methods must be devised to obtain the necessary condition of supersaturation in the solution. In substances of limited solubility use may be made of the common ion effect in which a soluble salt containing one of the ions of the salt to be crystallized is added to a saturated solution of that salt causing precipitation. A familiar example is the addition of hydrogen chloride to a saturated solution of sodium chloride, causing the sodium chloride to crystallize out of solution, the chloride ion, of course, acting as the common ion. This method is not applicable to the preparation of crystals of salts of very low solubility.

A limited number of substances virtually insoluble in water are appreciably soluble in mixtures of water and various organic solvents. A solution of these salts in water and the organic liquid may be prepared and crystallization of the salt accomplished by the controlled removal of the organic liquid.

Other methods include the controlled decomposition in solution of a soluble salt. This method is applicable when the salt to be crystallized is one of the decomposition products of and has an appreciably lower solubility than the salt originally placed in solution. Simple chemical precipitation may be accomplished by combining solutions of soluble salts, each of which contains one of the ions of the insoluble salt whose crystals are to be prepared. Although simple in theory, this last method is difficult to adapt to crystal growth and no record was found of the development of a technique which was even moderately successful.

It may be readily appreciated that most of the above methods may not be used in growing crystals of calcite simply because calcite does

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not possess the properties of which these methods were designed to take advantage. The solubility of calcite is 1.45×10^{-3} grams in a hundred grams of solution at 17° C. The carefully controlled evaporation of almost seventy liters of solution would thus be required to deposit one gram of the material. The insignificant change in solubility with temperature makes this method, too, impractical for the growth of calcite. Because of the low solubility of calcite the common ion effect may not be used to advantage nor is there any known organic solvent which, when combined with water, might dissolve a sufficient quantity of the material that slow extraction of the organic solvent might facilitate precipitation. Of the methods previously described only the decomposition reaction and the chemical precipitation appear to offer the possibility of adaptation to the growth of calcite and these are the only methods which are mentioned in the literature concerning crystal growth.

Although investigations concerning the artificial preparation of crystals have been conducted at an ever-increasing rate during the past hundred or more years, very little record exists of the development of methods by which crystals of calcite may be grown in the laboratory.

Buckley makes reference to the work of H. Vater in 1899 in preparing calcite crystals from solution by the slow conversion of calcium bicarbonate to calcium carbonate by heating the solution. The reaction is given by the following equation:

 $Ca(HCO_3)_2 \xrightarrow{heat} CaCO_3 + H_2O + CO_2$

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The growth was controlled by regulating the rate at which the carbon dioxide was permitted to escape from the system. The solubility of calcium bicarbonate at 100° C is 0.1660 grams in 100 grams of water, while that of calcium carbonate is 1.45×10^{-3} grams. Thus, the conversion of one liter of a saturated bicarbonate solution would yield nearly 1.22 grams of calcium carbonate.

Crystals of many minerals, including calcite, have been prepared through chemical precipitation by separating with a membrane solutions of soluble salts; each of which contains one of the ions of the mineral to be grown. As the solutions diffuse slowly through the membrane chemical reaction proceeds to produce crystals of the desired mineral. The membrane, however, soon becomes clogged with the insoluble precipitate and the resulting crystals do not attain more than microscopic size.

Since so little investigation has been conducted on methods of chemical precipitation in the artificial growth of calcite crystals and inasmuch as this method appears to offer one of the very few possibilities of application to the problem of growing calcite, it has been selected for further investigation insofar as it may be adapted to the growth of calcite. The methods employed and the results obtained will be discussed in subsequent sections of this thesis.

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APPARATUS AND METHODOLOGY

Two separate methods of effecting the precipitation of calcium carbonate from solution were employed and apparatus was assembled to adapt these methods to the growth of calcite crystals. The first method involved the precipitation of calcium carbonate from a solution of calcium hydroxide by the reaction of the solution with carbon dioxide. In the second method the carbonate was precipitated by the controlled mixing of solutions of calcium chloride and sodium carbonate. These two methods will subsequently receive detailed description and will be discussed separately, for the most part, throughout the remainder of this paper.

Precipitation with Carbon Dioxide

At 25° C the solubility of carbon dioxide is about 0.15 grams in one hundred milliliters of water, which is equivalent to a concentration of 0.034 moles per liter. The carbon dioxide and water unite chemically to form a dilute solution of carbonic acid (H_2CO_3) which ionizes in two steps as represented by the equations:

 $\frac{H_2^{00}_3 \longrightarrow H^+ + H^{00}_3^-}{(H_2^{00}_3)} = 3.5 \times 10^{-7}$

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$$\frac{(\text{H}^{+}) (\text{CO}_{3}^{--})}{(\text{H}^{0}\text{CO}_{3}^{--})} = 7.0 \times 10^{-11}$$

In calculating the carbonate ion concentration from the latter equation, the hydrogen ion and bicarbonate ion concentrations are found to be very nearly equal and will cancel in this expression. The carbonate ion concentration is, therefore, equal in value to the second ionization constant, namely, 7×10^{-11} mole per liter. Since the solubility product constant for calcium carbonate at 25° C is 8.7×10^{-9} mole per liter it is apparent that precipitation of calcium carbonate from a solution of a soluble calcium salt by the direct addition of carbon dioxide may not be accomplished unless the equilibrium can be shifted so as to produce a greater concentration of the carbonate ion.

The increase in concentration of the carbonate ion may be accomplished by lowering the hydrogen ion concentration through the addition of a base. Calcium hydroxide is the only compound which will fulfill the requirements of providing a source of calcium ions as well as furnishing the basic ions to lower the hydrogen ion concentration and is, therefore, the only calcium salt which, in solution, will combine with carbon dioxide to produce a precipitate of calcium carbonate.

The apparatus designed to adapt the above reaction to growing crystals of calcite (see Fig. I) consisted of a two hundred millimeter test tube with a sidearm opening near the top of the tube, this opening being connected by rubber tubing to a carbon dioxide generator constructed to

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Fig. I. Apparatus for precipitation by carbon dioxide

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maintain a constant pressure of the gas very slightly in excess of atmospheric pressure. The top of the test tube was closed by a two-hole rubber stopper through which the tip of a 125 milliliter separatory funnel extended into the tube about one inch. One end of a U-shaped section of small diameter glass tubing reached to the bottom of the test tube through the stopper, and was used to withdraw the used solution which collected in the test tube. The seed crystal was suspended by a piece of Chromel wire about one centimeter below the tip of the separatory funnel. The entire apparatus was clamped to a ring stand for support.

The seed crystals used in this investigation were small cleavage rhombohedrons of clear calcite. In activating the apparatus the air was swept from the test tube with carbon dioxide, the rubber stopper from which the seed crystal was suspended was fitted into place, and the stopcock of the separatory funnel which contained the calcium hydroxide solution was opened slightly to permit the solution to drop at a slow rate upon the seed crystal. Thus, the surface of the seed crystal was continuously coated with a film of the calcium hydroxide solution which reacted with the surrounding atmosphere of carbon dioxide to precipitate calcium carbonate. One distinct advantage of this method was that the chemical reaction occurred only in the thin film of solution at the surface of the seed crystal. It was anticipated that by keeping at a minimum the amount of solution reacting at a given time, the tendency for crystal nuclei to form could be kept at a low value and the greatest possible proportion of the precipitated calcium carbonate could be translated into growth upon the seed crystal.

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A series of nine trial runs of this apparatus were made with growth periods ranging from 24 hours to two weeks. During this period the apparatus was adjusted and modified as needed so as to provide a system whereby the process might continue over extended periods of time with a minimum of attention.

A bank of six of these units was set up using five hundred milliliter distilling flasks in place of the test tube. Carbon dioxide was provided by a single generator which was connected to the sidearm of the flasks by means of rubber tubing. Solution was supplied to the flasks from a 350 milliliter separatory funnel, and the rate of flow of the solution to each individual flask was controlled by adjusting a screw clamp placed upon the rubber tubing connecting the flask with the separatory funnel.

The seed crystals were carefully weighed and suspended in the flasks and the flow of solution to each flask was adjusted at a different rate. The process continued without interruption for a period of 18 days. At the end of this period the crystals were removed from the flasks and reweighed. The concentration of the calcium hydroxide solution was determined analytically and samples of the solution which collected in the bottom of each flask, having been protected by a thin layer of light oil from further reaction with the carbon dioxide, were analyzed to determine the amount of unreacted calcium hydroxide remaining in the solution.

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Precipitation by the Mixing of Solutions

This method involves the precipitation of calcium carbonate by the addition of calcium chloride to a solution of sodium carbonate, according to the reaction

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2 NaCl$$

By controlling the rate at which the solutions were combined, any degree of supersaturation relative to calcium carbonate could be obtained.

Theoretically, at a low degree of supersaturation few, if any, crystal nuclei should form. In practice, however, the initial mixing of the two solutions could not be accomplished with sufficient thoroughness to avoid local concentrations great enough to initiate crystal formation. Once crystallization has begun, it proceeds rapidly until all calcium carbonate present in the solution in excess of its normal solubility is precipitated as fine crystals. While it would appear that a state of supersaturation could not be maintained in the solution under these conditions, this is not true if the dimensions of the crystals thus formed lie within certain low size limits. These crystals are more soluble (supersoluble) than are the larger crystals and a condition of supersaturation is maintained until the small crystals are completely dissolved and the solution reaches a state of equilibrium with the precipitated material. The concept of the larger crystals growing at the expense of smaller ones in the same solution is a familiar one to most chemists, and frequent use is made of this principle in causing a precipitate to become coarser, thereby increasing the ease of handling.

It was noted that the time required for the settling of calcium carbonate crystals (prepared by the mixing of solutions of calcium chloride and sodium carbonate) decreased rapidly for several hours following the initial preparation, and continued to decrease noticeably for several days. The growth of these crystals, as indicated by the increased settling velocity, provided evidence that crystals sufficiently small to be supersoluble were formed in the mixing of these solutions. Thus, it would appear that the necessary state of supersaturation could be maintained.

In constructing the apparatus with which to adapt these principles to the artificial growth of calcite, it was recognized that, while the multitude of tiny crystals formed by the reaction were necessary in maintaining the supersaturation of the solution, their presence in the crystallizing vessel would cause considerable difficulty. For the purpose of carrying off these tiny crystals and preventing them, insofar as was possible, from settling on the seed crystals, it was considered desirable to have a constant flow of water through the vessel.

A two hundred millimeter test tube (see Fig. II) with sidearm opening near the top served as the crystallizing cell. Through a two-hole rubber stopper were inserted short lengths of small diameter glass tubing, each of which had the lower end drawn out to a reduced diameter and bent upward in the form of a hook. The longer of these tubes reached to the bottom of the test tube, while the lowest portion of the other reached a point about one inch above the bottom of the test tube. The shorter tube was connected by rubber tubing to a glass siphon

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Fig. II. Apparatus for precipitation by mixing of solutions

placed in a two liter bottle of the calcium chloride solution. The longer tube was connected through two glass "Y" tubes to the water tap by means of rubber tubing. The "Y" tube nearest the tap provided the inlet for the sodium carbonate solution, which was automatically withdrawn from a four liter beaker by means of a siphon connected to the "Y". The second "Y" tube served as an air bleed, the bubbles of air thus released at the bottom of the test tube aiding materially in mixing the solutions. The sidearm of the test tube served as an overflow and was equipped with a piece of rubber tubing to carry off the surplus solution. Flow of the solutions was controlled with screw clamps. The seed crystals were suspended on short lengths of Chromel wire within the test tube.

During preliminary runs with the apparatus it was noted that a hard coating of calcium carbonate formed upon objects with which the overflow solution came in contact, indicating that the solution was still supersaturated at this point. A second crystallizing cell in the form of a two hundred milliliter Erlenmeyer flask was, therefore, connected to the lower end of the overflow tube. The solution was carried to the bottom of the flask by a short piece of glass tubing extending through the twohole rubber stopper closing the neck of the flask. Escape for the solution was provided at the top of the flask by a second length of glass tubing which curved downward on the outside of the flask in the form of a siphon. The seed crystals were suspended in the solution on silk threads attached to the stopper.

Actual control of the degree of supersaturation was accomplished by regulating the rate of flow of the calcium chloride solution into the

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test tube. The concentration of the calcium chloride solution was determined analytically and the extent to which it was subsequently diluted was determined by measuring the total flow through the outlet during a given time interval. The flow of the sodium carbonate solution was not actually measured, but was maintained at a rate slightly in excess of that necessary to react with the amount of calcium chloride present in the solution at any time. Frequent checks were made on the solution escaping through the overflow tube to assure that the necessary level of carbonate ion concentration was being maintained. A number of separate runs were made with this apparatus at a variety of different degrees of supersaturation. The seed crystals were weighed prior to and at the end of each run to determine the amount of growth, and frequent microscopic examinations of the growing crystals were made to determine the nature of the growth.

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RESULTS

Precipitation with Carbon Dioxide

An initial run of 18 days duration was made with the bank of six units previously described at rates of solution flow ranging from 2.1 to 8.3 milliliters per hour. The seed crystals were removed from the flasks at the end of this period and were reweighed after being cleansed to remove the coating of small crystals (formed by the chemical reaction) which adhered to the surface. Results of this run indicated that solution of the seed crystals had occurred, the loss of weight varying inversely with the rate of flow of the solution over the crystal. Although all of the crystals were somewhat reduced in weight, the results suggested that growth might be expected to occur at rates of flow higher than those which were used. Accordingly, a second series of runs was made at rates varying from 5.9 to 47.6 milliliters per hour. Because of the large volume of solution required to maintain a flow at these rates a two liter bottle with a siphon was substituted for the separatory funnel and the period of time over which the run was made was reduced to twelve days.

The crystals were cleansed and weighed as previously described and it was found that growth occurred at rates of flow greater than twenty milliliters per hour. The results of the two runs were combined and are presented in Table I. The variation in change of weight of the crystal with rate of solution flow is shown graphically in Figure III.

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Fig. III. Variation in rate of growth with rate of solution flow

It was found that the relationship most closely approached linearity when the square root of the change in weight in milligrams was plotted against the log of the rate of flow in milliliters per hour, and Figure III has been prepared in this manner.

Precipitation by the Mixing of Solutions

Preliminary runs with this apparatus indicated an appreciable variation in the rate of growth with time and a series of determinations was planned by which this variation might be measured. The calcium chloride solution was standardized and found to be 0.1560 molar. The total flow of solution through the overflow tube was measured (150 milliliters per minute) and the amount of calcium chloride solution which must enter the crystallization tube to maintain one degree of supersaturation of calcium carbonate in the solution was calculated as sixteen milliliters per hour.

A series of runs was made at one degree of supersaturation over periods of twelve, twenty-four, and sixty hours. At the end of each period the crystals were removed, cleansed and reweighed, and the interior of the apparatus was rinsed with dilute hydrochloric acid to remove all traces of calcium carbonate. The series of runs was repeated at two and five degrees of supersaturation and the average increase in weight of the three seed crystals used in each run is shown graphically in Figure IV.

The crystals in the Erlenmeyer flask continued to grow over a somewhat longer period of time and did not show a significant change in rate of growth with change in supersaturation. The amount of growth occurring on these crystals under varying conditions is given in Table III and the average of these results has been used in preparing Figure V.

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Fig. IV. Variation in rate of growth with time



Fig. V. Variation in rate of growth with time

CONCLUSION

Precipitation with Carbon Dioxide

While growth upon the seed crystals occurred at rates ranging upward from approximately 20 milliliters per hour, this method obviously does not offer a practical solution to the problem of growing crystals of calcite. The results indicate that roughly 400 liters of saturated calcium hydroxide solution (containing 660 grams of $Ca(OH)_2$) flowing at a rate of 40 milliliters per hour for 400 days would be required to increase the weight of the seed crystal by one hundred milligrams.

Probably the major weakness in this method is a result of the low solubility of the calcium hydroxide. The reaction between the carbon dioxide and calcium hydroxide is virtually instantaneous and the formation of tiny crystals of calcium carbonate is apparent in the clouding of the solution as it drops into the atmosphere of carbon dioxide. While the hydroxide ion is present in the solution, the reaction

 $Ca(OH)_2 + H_2CO_3 \longrightarrow CaCO_3 + H_2O$

proceeds. When the hydroxide ion is depleted by this reaction the concentration of carbonic acid in the film of solution surrounding the crystal increases and the following reaction occurs between the solution and the crystal:

$$CaCO_3 + H_2CO_3 \longrightarrow Ca(HCO_3)_2$$

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At 20° C the solubility of calcium bicarbonate is 0.1840 grams in 100 grams of water while that of calcium hydroxide is 0.165 grams in 100 grams of water. If a drop of the solution remained on the surface of the crystal sufficiently long for the second reaction to reach completion, a net loss of as much as 190 milligrams of calcium carbonate from the seed crystal per liter of solution might be expected to occur.

The greater part of the calcium hydroxide in solution appears to be precipitated in the form of crystals which are not sufficiently small to be supersoluble. It must be concluded that an appreciable degree of supersaturation cannot be maintained in the solution surrounding the seed crystal and that growth at any but an exceedingly slow rate is not possible under these conditions.

Precipitation by the Mixing of Solutions

Although a high initial rate of growth was obtained, certain limiting conditions must be overcome before this method may be considered successful for growing crystals of calcite. A deposit of small crystals of calcium carbonate accumulated rather rapidly on the inside of the crystallization tube. This deposit on the interior of the tube presented a surface upon which growth might occur that was many times greater than the surface area of the seed crystal, and tended to absorb most of the growth potential of the solution. In addition, a soft crust of the small crystals formed in the solution tended to collect on the surface of the seed crystal, effectively insulating it against further growth.

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In the Erlenmeyer flask connected to the overflow tube these conditions developed less rapidly and as a result the growth continued over a somewhat longer period. Due largely to previous settling of the suspended particles, the solution flowing through the flask remained essentially clear at all degrees of supersaturation. Although the formation of a carbonate coating on the sides of the flask was slower to develop and the growth period was correspondingly increased, no method was found to completely eliminate this difficulty and a period of growth of more than a few days duration could not be attained.

SUGGESTIONS FOR FUTURE STUDY

Calcite is a mineral of considerable geologic importance, and the study of the conditions under which it will crystallize from solution may be applied directly to the formation of limestone by chemical precipitation and to the cementation of various sediments.

The calcium carbonate-carbon dioxide equilibrium is significant in both the solution and deposition of calcite under conditions found near the surface of the earth. A successful study of this equilibrium would represent an important contribution to the knowledge concerning the actual mechanics involved in these processes.

In the opinion of the writer the most fruitful avenues for further investigation are:

- (1) Continued study of the method of growth involving the mixing of solutions with the aim of reducing or eliminating the factors which limit the length of the growth period. The use of substances which would serve as mineralizers may be an appreciable aid toward achieving this end.
- (2) The rate of increase in the permeability of limestones caused by the migration through them of water carrying dissolved carbon dioxide at various pressures. This might be related to the redeposition of calcium carbonate in unconsolidated sediments upon release of pressure.

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A PPENDIX

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RESULTS OF PRECIPITATION BY CARBON DIOXIDE METHOD

Time	Total Soln. Flow Per		Change in Wt. (mg.)		Sq. Root of
(Days)	(ml.)	Hr. (ml.)	Total	Per 6 Days	Change Per 6 Days
18	910	2.1	- 93 . 0	-31	5.57
18	1,030	2.4	-72.0	- 24	4.9
18	1,300	3.0	-53.0	-17.7	4.20
18	1,860	4.3	-30.0	- 9.3	3.05
18	3 ,010 `	7.2	-12.0	- 4.0	2.0
18	3,540	8.3	- 9.0	- 3.0	1.65
12	1,700	5.9	-11. 5	- 5.8	2.39
12	3,600	12.5	- 1.5	7	•84
12	5 ,320	18.5		Not Measurab	le
12	7 ,37 0	25.6	1.0	•5	.7
12	11,210	38.9	1.5	.7	. 84
12	13,700	47.6	5.0	2.5	1.6

RESULTS OF PRECIPITATION BY MIXING OF SOLUTIONS

Degrees of Supersaturation	Time (Hrs.)	Increase in Wt. (mg.)	Av. Increase in Wt. (mg.)
l	12	2.8 3.4 3.0	3.1
	24	4.2 4.2 3.8	4 . l
	60	3.8 4.2 4.4	4.1
2	12	3•4 4•0 3•6	3.7
	24	4.8 4.4 3.8	4.3
	60	4.6 4.6 4.0	4•4
5	. ¹²	6.2 5.2 5.8	5.7
	24	6 .2 5.8 6.6	6.2
	60	6.2 5.9 6.2	6.1

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TABLE III

GROWTH OF SEED CRYSTAL IN ERLENMEYER FLASK

2.0	4.3	Average 6.6	7.2	7.5
2.0	4.4	7.0	7.4	7.7
2.0	4.2	6.2	7.0	7.4
1.8	4.2	6.6	7.2	7.4
12	24	60	96	156

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Time (Hrs.)

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REFERENCES

- Buckley, H. E. (1951) <u>Crystal Growth</u>, New York, John Wiley & Sons, Inc., passim.
- 2. Hogness, T. R. and Warren Johnson (1947) <u>Qualitative Analysis and</u>. <u>Chemical Equilibrium</u>, 2d. ed. New York, Henry Holt & Co., pp. 163-165.
- Pierce, W. C. and E. L. Haenisch (1948) <u>Quantitative Analysis</u>,
 3d. ed. New York, John Wiley & Sons, Inc., Ch. 18 & 19.







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