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CORRELATION OF CRYSTAL GROWTH RATES IN SUPERSATURATED SOLUTIONS

BY

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A THESIS
SUBMITTED TO THE FACULTY OF
THE DEPARTMENT OF CHEMICAL ENGINEERING
OF
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1955

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________

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NEWARK, NEW JERSEY
JUNE 1955

PREFACE

In the study of crystal growth, a large amount of work has been done to determine growth equations. Two examples of this work are the Hixson and Knox mass transfer coefficient equation (1) and the McCabe and Stevens growth rate equation (2).

Hixson and Knox (1) have presented a correlation expressing the mass transfer coefficient for a single crystal as a function of, V, the velocity of the solution past the crystal, D_m, diffusivity and, U, viscosity.

The work of Hixson and Knox (1) would predict that the rate of orientation at the crystal face is a contributing factor to the over-all rate, over the entire range of velocities investigated.

McCabe and Stevens (2) presented a simple empirical correlation for the rate of growth of copper sulfate pentahydrate as a function of, V, the velocity of the solution past the crystal, and, r_i, the interfacial growth.

It is the purpose of this paper to extend the scope of the McCabe and Stevens (2) correlation to cover at least one other crystal system and to investigate the influence of diffusion with regard to the crystal growth.

Preface (Continued)

It is the further purpose of this paper to check the influence of viscosity and density of solution on crystal growth, and the magnitude of influence of orientation rate versus velocities of solution past the crystal. The orientation rate exhibited a constant effect over the velocity range studied by Hixson and Knox (1), which is shown by the displacement of $CuSO_4$ and $MgSO_4$ plots. The mass transfer equations for these two systems are shown later on.

Hixson and Knox (1) used the viscosity and density terms throughout their mass transfer correlation equations. McCabe and Stevens (2) assumed the factors of viscosity and density throughout their series of runs. Therefore in this study, the quantities of viscosity and density will be verified with reference to their effect on crystal growth.

ABSTRACT

This investigation has shown that crystals of copper sulfate and magnesium sulfate when grown in supersaturated solutions exhibit a growth rate according to the following equation:

$$R_L = 5.0 \ (\Delta C D_m)^{\frac{1}{\rho \upsilon}} \ V_s^{.292}$$

where, R_L, is the growth rate in Microns/min, is the change in concentration, D_m, the diffusivity coefficient, , density of solution, U, viscosity and V_s, solution velocity past the crystal.

The equation shown demonstrates that a mass transfer process is taking place from the solution to the crystal surface, and that within the velocity range studied, there was no effect shown by the interface orientation rate.

In a crystallizer where there is a mixture of crystals, the larger crystals will grow faster than those of a smaller size due to its higher relative solution velocity.

Crystal growth is dependent upon the other factors described in conjunction with the formulae, and the analogy between these factors is described in the main paper.

ACKNOWLEDGEMENTS

Professor George C. Keeffe, Newark College of Engineering, for his aid in determining the correlation and obtaining equipment.

Dr. W. L. McCabe, Brooklyn Polytechnic Institute, for his discussion on crystal size determination and rate of orientation.

Mr. Frank Kroll, Steel & Alloy Tank Company, Newark, New Jersey, for the manufacture of the crystal seed holder.

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INTRODUCTION

Work previously has been done on $CuSO_4$ and $MgSO_4$ systems by Hixson and Knox (1) and on $CuSO_4$ by McCabe and Stevens (2). The writer adhered to McCabe and Stevens (2) procedure with reference to the conditions and measurements, but used equipment of similar design to that of Hixson and Knox (1).

Other investigators in this field are:

Marc (11) who found out that above a certain rate of agitation there would be no further rate of growth.

Noyes and Whitney (12) did work on the rate of solution of Benzoic Acid in water. They found that this is dependent upon a diffusional process and on the rate of agitation.

Berthoud (13) and Valeton (14) each independently developed a theory of crystal growth to the rate of diffusion of the material in solution to the crystal surface.

Van Hook (6) (7) did work on the rate of crystal growth in sucrose solutions.

It is noted in the literature that for crystal growth the crystal must have a lower thermodynamic potential after crystallization than before. If it did not, the crystal

Introduction (Continued)

would dissolve instead of growing. It is common knowledge that the solution is supersaturated prior to crystal formation.

Growth is feasible through the process of a precipitating substance being transferred from a supersaturated solution to an interface film and rearranging itself into a specific crystal lattice in order for growth to take place. This growth is dependent upon the degree of supersaturation; i.e., its thermodynamic potential, the formation of the seed crystal, the interface effect between the crystal and crystal solution, the formation of a crystal lattice and the solution velocity relative to the growing crystal.

The process of crystallization with regard to the shape of the crystal which is growing does not conform to the thermodynamic equilibrium of a crystal with its saturated solution, and Hixson and Knox (1) have noted in their studies variances in the order of nineteen percent (19%) for copper sulfate pentahydrate and thirty-three percent (33%) for magnesium sulfate heptahydrate.

McCabe and Stevens (2) propose the following empirical equation for the growth of copper sulfate pentahydrate:

$$\frac{1}{r_g} = \frac{1}{r_o + \beta V} + \frac{1}{r_i}$$

Introduction (Continued)

where r_g is the rate of growth in microns per unit time of a crystal in an agitated solution at constant supersaturation. This is equated as the relative velocity, u, between the crystal and its solutions, the interfacial growth rate, r_1, and the growth rate at zero velocity, r_o.

The Hixson and Knox (1) equation is a mass transfer equation through which a study was made to determine the mass transfer coefficient for crystal growth. The work was compared with other mass transfer coefficients and with heat transfer coefficients of the Chilton-Colburn analogy.

The mass transfer coefficients for copper sulfate were given by:

$$\frac{F_d D_e}{\beta D_m} = 0.29 \left(\frac{D_e V \rho}{\mu} \right)^{.6} \left(\frac{\mu}{M_m D_m} \right)^{.3}$$

and for magnesium sulfate:

$$\frac{F_d D_e}{\beta D_m} = 0.48 \left(\frac{D_e V \rho}{\mu} \right)^{.6} \left(\frac{\mu}{M_m D_m} \right)^{.3}$$

Van Hook (7) did work on the crystal growth of sucrose and he confirmed that the rate controlling step in sucrose crystal growth is the surface reaction not the diffusivity.

McCabe and Stevens (2) state that the growth rate is not effected directly by the crystal size but that the rate

Introduction (Continued)

of growth at low velocities is determined by the diffusivity of the mass transfer process of material from the solution to the crystal surface. Yet as velocity increases, the rate of growth diminishes, thus making the interfacial growth rate rate determining.

This is better illustrated by the following:

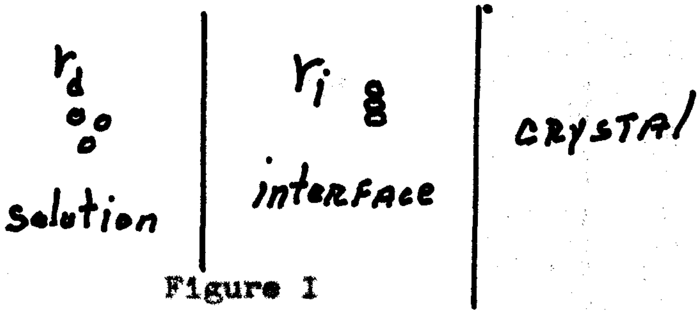


Figure I

As shown in Figure I, when, r_d, the diffusivity rate is less than r_i, the interfacial or orientation growth rate, then the diffusivity is rate determining with respect to crystal growth.

The term, r_d, diffusivity rate, is directly effected by velocity. For as the molecules are transferred from the solution to the interface for orientation into the crystal lattice, new molecules must diffuse through the solution to the interface in order for growth to take place. Consequently, the velocity of the solution past the crystal will increase the potential of a molecule of material replacing one which is being orientated at a faster rate at a higher velocity than one at a lower velocity.

When the diffusivity is greater than the rate of interface orientation, then the rate determining factor is that of, r_i, the interfacial growth rate. Using the same analogy when there are more molecules present than can be orientated, the interfacial rate is the one which is the slowest and is rate determining. Velocity is negligible at and above this point.

The determination of this point, i.e., $r_d = r_i$, is of high interest to the manufacturers of crystallizers, for when the solution velocity no longer plays an important part, any increase in agitation rate would be uneconomical.

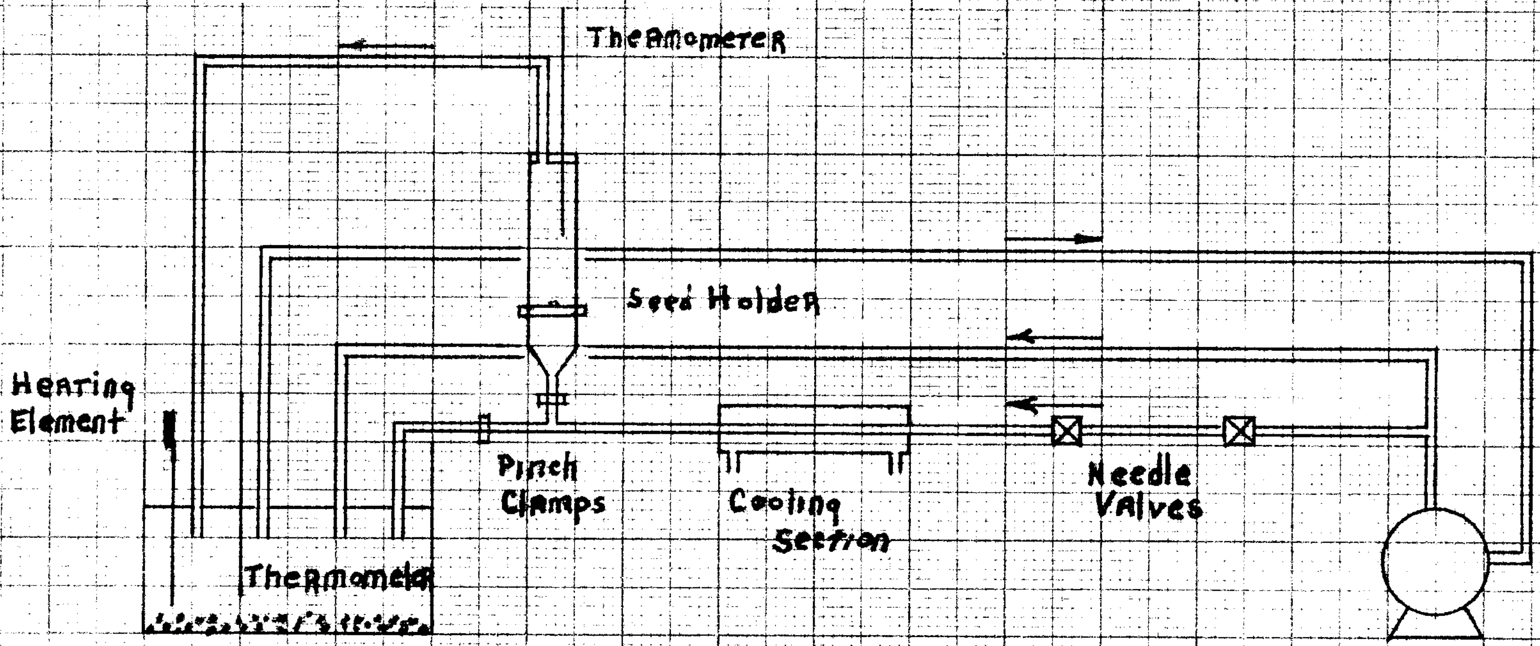
It was therefore proposed that higher solution velocities be attempted to possibly determine the point where $r_d = r_i$.

In these experiments, rates of growth were made on a single crystal supported by a crystal seed holder, through which flowed a constant supersaturated solution for all runs. A correlation for crystal growth rate was determined for the $CuSO_4 \cdot 5H_2O$ and $MgSO_4 \cdot 7H_2O$ in terms of concentration, velocity and rate diffusion coefficients.

Introduction (Continued)

With reference to the viscosity and density, these factors played an important part in the correlation even though they remained constant with regard to the temperature throughout the series of runs on $CuSO_4$ and $MgSO_4$ solutions.

FIGURE II



SCHEMATIC DIAGRAM

OF

APPARATUS

EXPERIMENTAL

The equipment consisted of

(1) An ECO stainless steel, positive displacement, rubber impellor pump.
(2) Stainless steel lines.
(3) A glass section for housing the crystal holder and thermometer.
(4) A crystal holder of 325 mesh stainless steel.
(5) A bath for holding the saturated solution including a heating element and thermometer.
(6) A cooling section for supersaturation of the solution prior to the crystal seed holder.
(7) A by-pass both for the pump and the crystal seed holder.

This allows flexability in the equipment for controlling the small flows and ease in obtaining equilibrium conditions prior to a run.

It was noted in the previous works, both on inorganic and organic compounds, that impurities will either increase or decrease the crystal growth. In this vein, precautions were taken to insure purity by the usage of C.P. substances in distilled water.

The equipment was cleaned by HCl and HNO_3 acid solutions, then numerous water rinses and finally, two rinses with distilled water.

The crystals were measured by the aid of a microscope with a calibrated eyepiece and held in a small test tube prior to use. The eyepiece was in turn calibrated by means of a stage micrometer graduated to a 0.01mm or 10 microns. Single crystals were used in all runs. They were measured in microns and orientated to obtain the straight side of the crystals. This follows the method of McCabe and Stevens (2) with regard to crystal size determination. Copper sulfate pentahydrate is triclinic and magnesium sulfate heptahydrate is rhombic. With proper selection of straight-sided samples, several measurements of the length and width of the crystal were taken with the crystal in various oriented positions. Crystal size was obtained by the square root of the product of these two measurements. The size of the crystals was kept on the initial measurement to within the 700 to 1500 microns for ease and accuracy of measurement.

A run was made by obtaining standard conditions which were 28°C in the saturator and 27°C in the crystal seed holder. The velocity was determined by weight measurements which were taken during the run and averaged to take into consideration any pump fluctuations which might have occurred. Thus knowing the diameter of the crystal holder and the mass velocity, the average velocity past the crystal can be determined. It was thought to be the most satisfactory way of measuring velocity though more cumbersome than previous methods. Once the conditions were met, the crystal holder was by-passed -- opened and the seed crystal placed in position. By closing the holder and by-pass, the solution would again pass through the crystal holder over the seed crystal thus commencing a run.

The length of the run was held constant at thirty (30) minutes. At the end of this period of time the crystal was removed, washed in acetone, saturated with the specific salt of the crystal and returned to its specific test tube for remeasurement.

To determine saturated conditions, a crystal, usually of the 200 mg variety, was placed in the seed holder and a run of ten (10) minutes taken. If the crystal lost weight, the temperature was raised to 30°C for thirty (30) minutes and again returned to standard conditions. This procedure was repeated until growth was noted by an increase in weight of the crystal. Therefore at this time, a specific velocity was set in and a run was taken.

It is interesting to note that to obtain a saturated solution may take from three (3) to four (4) hours since we wish to have a solution free from seed crystals. A filter would become blocked and throw off the velocity from its set rate.

Twenty-one (21) runs were made on copper sulfate pentahydrate and fourteen (14) runs were made on magnesium sulfate heptahydrate, but only thirteen (13) and eight (8), respectively, were used. The remainder of the runs were discarded either for ambiguous results or lost crystals. It is interesting to note that three (3) crystals of the magnesium sulfate heptahydrate reverted to the anhydrous form due to the writer not measuring them for four (4) days after growth. Hence the procedure of measurement within eight (8) hours was adopted during the remainder of the eleven (11) runs.

The crystal seed holder was so constructed that all of the solution must pass through the seed holder, consequently giving better control over the velocity of solution moving past the crystal.

Experimental (Continued)

Velocity Determination

The 325 mesh woven wire screen was obtained from the Newark Wire Cloth Company of Newark, New Jersey, and from their "Catalog E", page 42, under "Twilled Weave", the following information is found:

Meshes Per Linear Inch	Diameter of Wire	Width of Opening	Open Area Per cent
325 x 325	0.0356 mm	0.0432 mm	30

Therefore, knowing the area in square centimeters of the crystal seed holder (10.8 sq cm) and obtaining thirty (30) per cent as flowable area, one can determine the velocity from the mass flow which has been weighed in grams.

COMPARISON OF CRYSTAL SIZE

In general crystal size does not effect crystal growth; but in order to eliminate the possible effect of crystal size, crystals of comparative size were used in the crystal growth determinations for both the copper and magnesium sulfate runs.

Copper Sulfate Pentahydrate Microns	Magnesium Sulfate Heptahydrate Microns
1507	1274
1489	1208
1469	1169
1405	1153
1362	1081
1324	992
1045	889
1015	875
965	
790	
785	
737	
714	
R_L Aver. 1132	R_L Aver. 1080

The average size of the copper sulfate crystals compare favorably with that of the magnesium sulfate crystals. The difference between the average size is 52 microns; and when compared with crystals whose size is determined by sieve analysis, the difference is greater, for example:

Newark Wire Cloth, Catalog E, Pg. 52
U.S.S.-A.S.T.M. Designations for Testing Sieves

Number 18	1000 Micron
" 16	1190 "
" 14	1410 "
" 12	1680 "

Comparison of Crystal Size (Continued)

As shown, the differences between sieve number 18 and 16, 16 and 14 and 14 and 12 are 190, 220 and 270 microns respectively.

It is possible to obtain crystals of a larger size than that of the known sieve size due to the shape of the crystals. The average crystal, being rectangular in shape, could have a length two or three times its width. The width being equal to the sieve opening and, consequently, giving a crystal greater in size than that which is supposed to be determined by the opening in the sieve.

Measurements were made by orientation to obtain the straight side of the crystal. The length and the width of the sample were obtained several times with different orientated positions. The average size was then determined by taking the square-root of the product of the length and width of the crystal, and the size determined was the length of one side of a cube. It is felt that this is a better method than that of obtaining an equivalent diameter of a sphere by weight measurement since a cube more closely resembles the crystalline shape of the crystals used in this work.

The size of the crystals used in this work is well above the critical size so that when in a saturated solution they will grow and not dissolve.

DETERMINATION OF RATE OF ORIENTATION

McCabe and Stevens (2) state that the rate of orientation of the precipitated material at the crystal surface is not rate determining at the velocities which were used in their experiment. In order to determine whether this was true, the author took a greater velocity span than that of McCabe and Stevens (2).

Namely:

Author	Velocity
McCabe and Stevens	0 to 3.6 cm/sec
Palme	0 to 11.68 cm/sec

It is shown on Figure III that the rate of growth is determined by a function of velocity and not the rate of orientation of transferred material at the interface of the crystal. Therefore, for either system on the Log-Log Plot, straight lines were obtained showing that velocity was rate determining due to an increase of R_L per unit velocity increase.

CORRELATION DETERMINATION

In the postulations of a simple equation, the results of the experimentation were tabulated and plotted, Tables II, III and Figure III, respectively. It is shown here that the rate of growth of magnesium sulfate heptahydrate is higher per unit velocity than copper sulfate pentahydrate.

In order to bring these two lines together, the rate of growth (R_L) of copper sulfate pentahydrate and magnesium sulfate heptahydrate were divided by their differences in solubility obtained from Figures VII and VIII, respectively.

$$\frac{R_L}{C_{T_s} - C_{T_{ss}}} = \frac{R_L}{\Delta C}$$

Where $T_s = 28^\circ C$ and $T_{ss} = 27^\circ C$

For $CuSO_4 \cdot 5H_2O$ $\quad C = 0.63$

For $MgSO_4 \cdot 7H_2O$ $\quad C = 1.04$

The results are found in Tables IV, V and Figure V.

In reviewing Figure V, it is plain that the rate of growth, R_L, is a function of the solution concentration. This is not the complete function.

Since results have been obtained which indicate that velocity is the rate-controlling factor (Figure III), we therefore know that it alone will not give us a correlation. We also know that the amount of supersaturation, or driving force, is a function of R_L, and even though related to velocity, another variable or variables is missing.

Correlation Determination (Continued)

Reviewing the literature, the term diffusivity, D_m, viscosity, U, and density, ρ, appeared both in the work of Hixson and Knox (1) and of McCabe (3). In reviewing McCabe (3) with regard to the theory of nucleation, he discussed the work of Becker, R. (15) in which the diffusivity term was used as a power function incorporated with a constant and temperature in the empirical equation for nucleation.

Since temperature is constant for both solutions, our analysis is one of velocity, concentration, diffusivity, viscosity and density. The change in concentration, Δc, is the amount of material that can be precipitated and controlled by the velocity as the driving force. This is not influenced by the interfacial reaction, which is assumed to be of such magnitude as not to influence a simple equation; and the product of Δc, change in concentration and diffusivity, D_m, were raised to the reciprocal of the product of viscosity and density. This can be interpreted as the resistance of solution against molecular diffusion, and the term $R_L/(\Delta c D_m)^{\frac{1}{\rho U}}$ versus velocity was obtained as shown on Tables IV and V for both systems and plotted as shown in Figure VI. A simple equation was obtained for a straight line function on a Log-Log plot where:

Correlation Determination (Continued)

$$\text{Log } x = a + b \log y$$

$$\frac{\text{Log } R_L}{(\Delta C\ D_m)^{1/\rho u}} = a + b \log V_s$$

$$R_L = a(V_s)^b(\Delta C\ D_m)^{1/\rho u}$$

and upon calculation

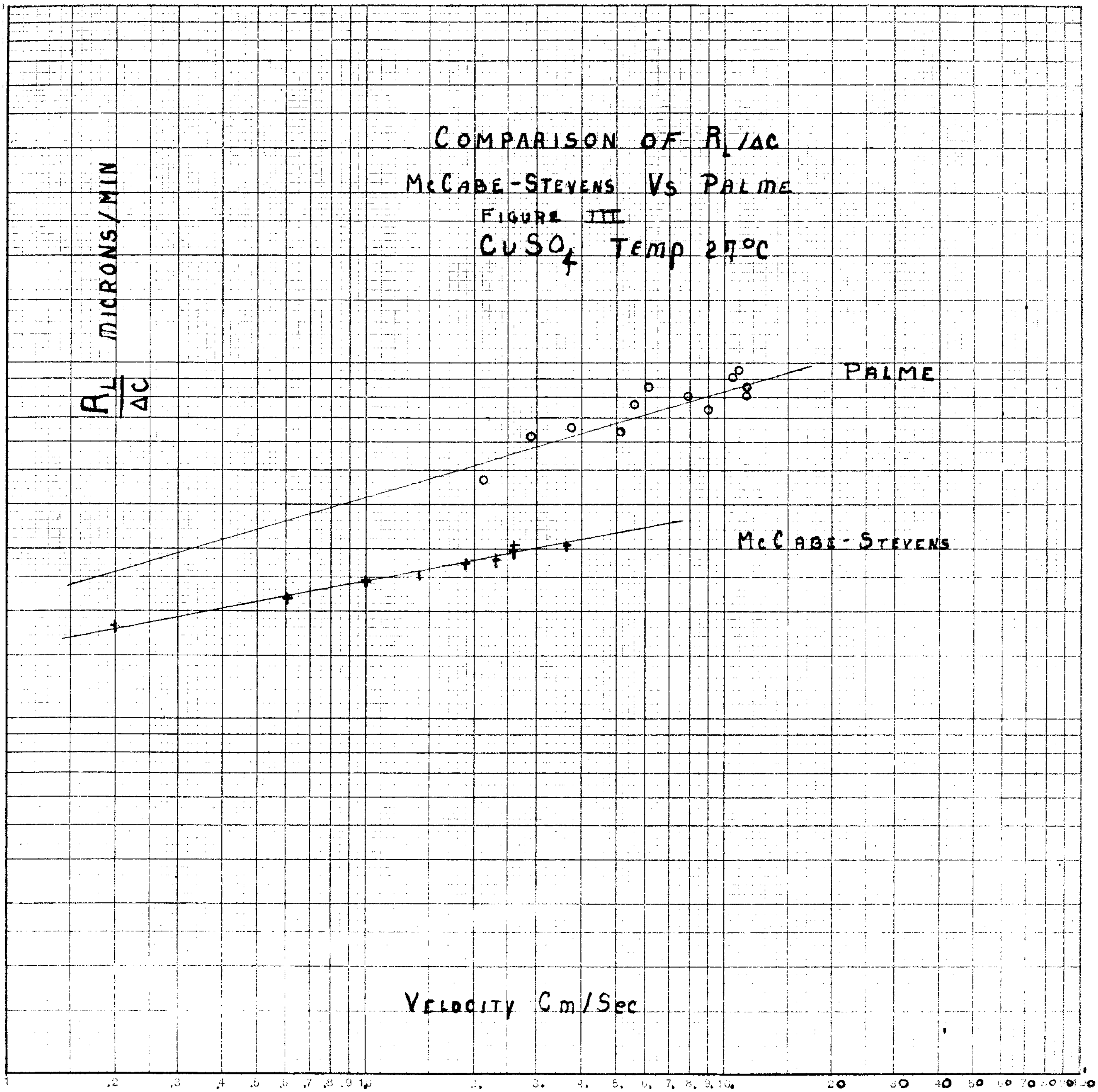
$$R_L = 5.0\ (\Delta C D_m)^{1/\rho u}\ (V_s)^{.292}$$

TABLE I

SUMMARY McCABE-STEVENS (2) DATA

Copper Sulfate Pentahydrate

Velocity cm/sec.	Ave. Crystal Size Microns	Growth Rate R_L microns/min	$R_L/\Delta c = .63$ microns/min
0.2	740	1.16	1.83
0.6	720	1.41	2.24
1.0	720	1.53	2.43
1.4	720	1.61	2.55
1.9	730	1.71	2.71
2.3	720	1.80	2.86
2.7	730	1.92	3.04
2.7	720	1.85	2.93
3.6	730	1.92	3.04


COMPARISON OF $R_L/\Delta C$

McCABE-STEVENS Vs PALME

FIGURE III

$CuSO_4$ Temp 27°C

TABLE II

Run	S_1 Microns	V_s cm/sec	S_2 Microns	R_L Microns/min	$R_L/\Delta c$ = .63 Microns/min
1	790	0	825	1.17	1.86
2	1362	3.77	1486	4.13	6.63
3	1324	5.60	1470	4.87	7.73
4	1045	2.23	1131	2.87	4.71
5	1489	7.96	1542	5.10	8.09
6	750	8.54	Lost Crystal		
7	977	2.49	812	Crystal Dissolving	
8	1507	11.52	1668	5.37	8.52
9	1469	5.13	1590	4.06	6.44
10	976	4.67	983	Lost Temp. Control	
11	706	2.77	Lost Crystal		
12	1405	9.00	1545	4.67	7.40
13	965	2.90	1092	3.93	6.23
14	785	6.16	977	5.40	8.56
15	880	5.77	Lost Crystal		
16	737	11.00	916	5.94	9.42
17	840	13.60	Lost Crystal		
18	988	10.89	1061	Not usable	
19	714	10.55	887	5.77	9.15
20	1015	11.60	1186	5.70	9.04
21	1127	0	Flask toppled, lost solution		

Copper Sulfate

Time 30 Minutes
T_s = 28°C T_{ss} = 27°C

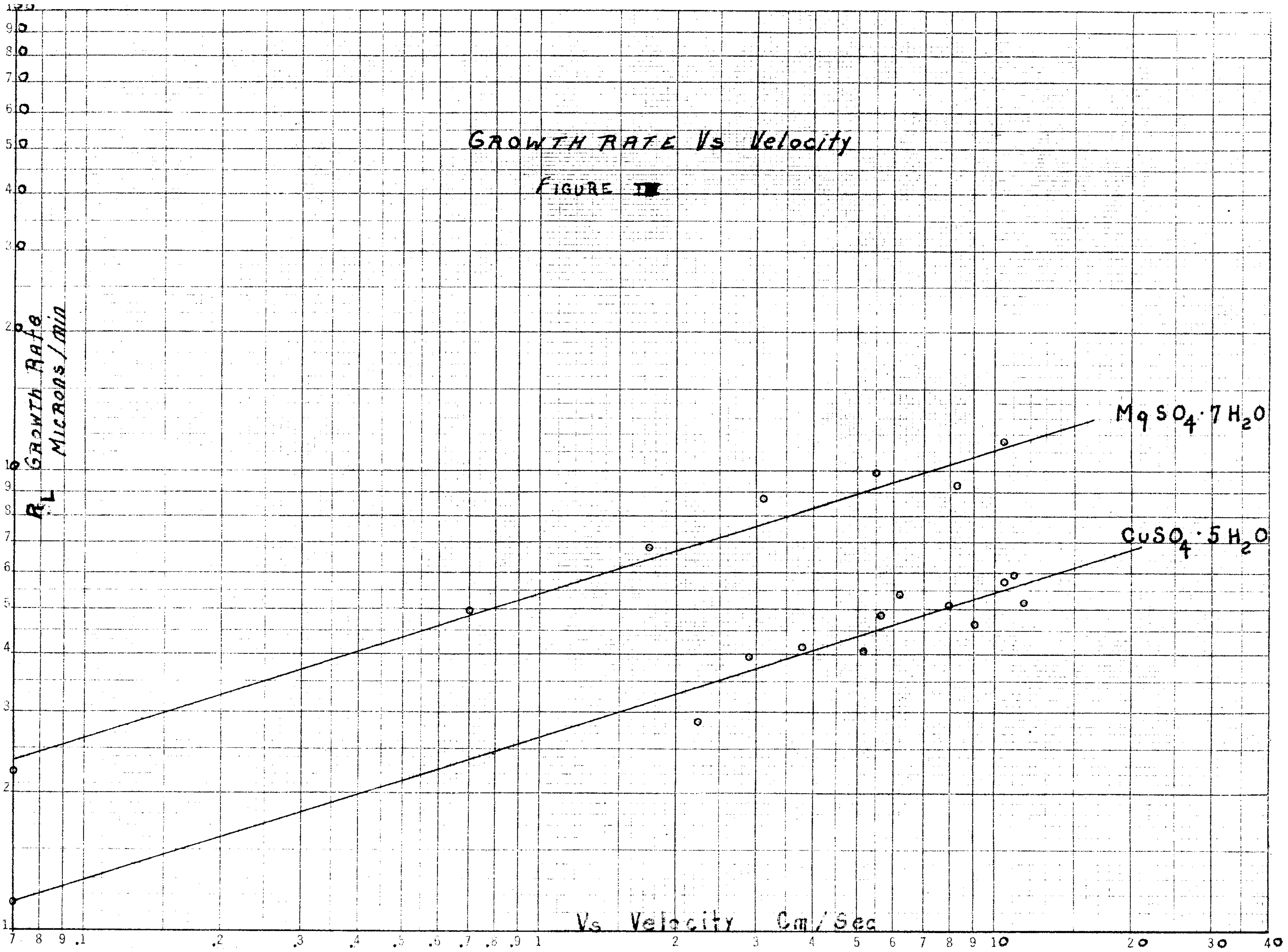
TABLE III

Run	S_1 Microns	V_s cm/sec	S_2 Microns	R_L Microns	$R_L/\Delta c$ = 1.04 Microns
1	1081	0	1147	2.20	2.11
2	1169	0.70	1318	4.97	4.76
3	992	2.26	1198	6.87	6.60
4	875	5.54	1171	9.87	9.47
5	1262	6.37	Crystal Anhydrous		
6	1015	8.67	Crystal Anhydrous		
7	976	9.62	Crystal Anhydrous		
8	1208	1.73	1412	6.80	6.54
9	889	3.10	1148	8.64	8.30
10	1076	5.70	Lost Crystal		
11	1153	8.17	1430	9.23	8.87
12	972	4.62	Lost Crystal		
13	1216	6.77	Lost Temp. Control		
14	1274	10.55	1622	11.60	11.15

Magnesium Sulfate

Time 30 minutes

T_s = 28°C T_{ss} = 27°C



GROWTH RATE Vs Velocity

FIGURE III

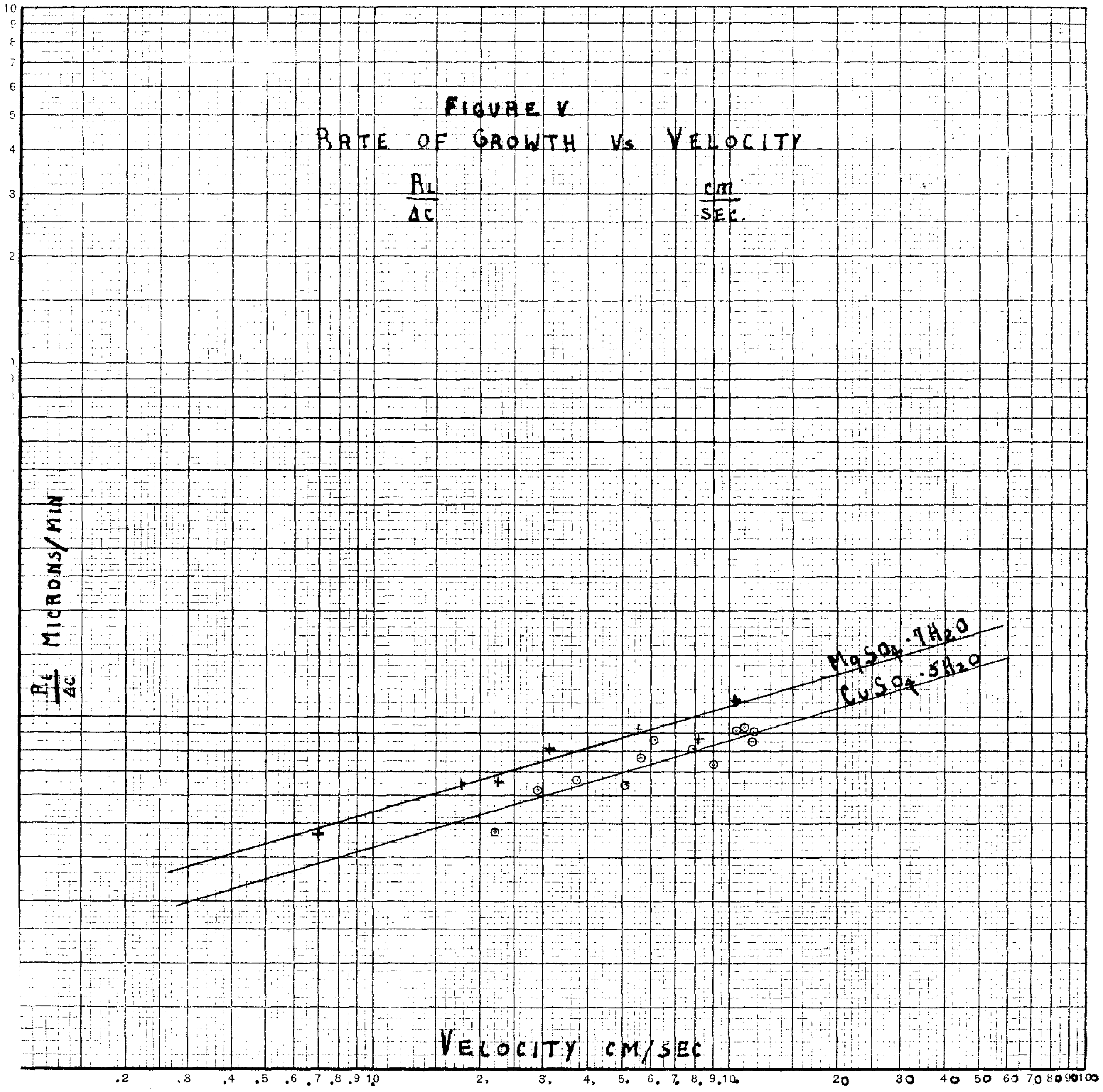


FIGURE V

RATE OF GROWTH Vs VELOCITY

TABLE IV

Copper Sulfate Pentahydrate

Summary

Run	Velocity cm/sec V_s	Crystal Growth Microns/min R_L	Crystal Growth Microns/min $R_I/(\Delta C D_{12}) \rho v$
1	0	1.17	2.09
2	3.77	4.13	7.37
3	5.60	4.87	8.70
4	2.23	2.87	5.13
5	7.96	5.10	9.10
8	11.52	5.37	9.60
9	5.13	4.06	7.25
12	9.0	4.67	8.35
13	2.9	3.93	7.02
14	6.16	5.40	9.65
16	11.0	5.94	10.60
19	10.55	5.77	10.32
20	11.68	5.70	10.20

TABLE V

Magnesium Sulfate Heptahydrate

Summary

Run	Velocity cm/sec V_s	Crystal Growth Microns/min R_L	Crystal Growth Microns/min $R_L/(\Delta c\, D_m)^{\frac{1}{\rho v}}$
1	0	2.20	2.02
2	0.70	4.97	4.60
3	2.26	6.87	6.35
4	5.54	9.87	9.12
8	1.73	6.80	6.28
9	3.10	8.64	7.97
11	8.17	9.23	8.54
14	10.55	11.60	10.72

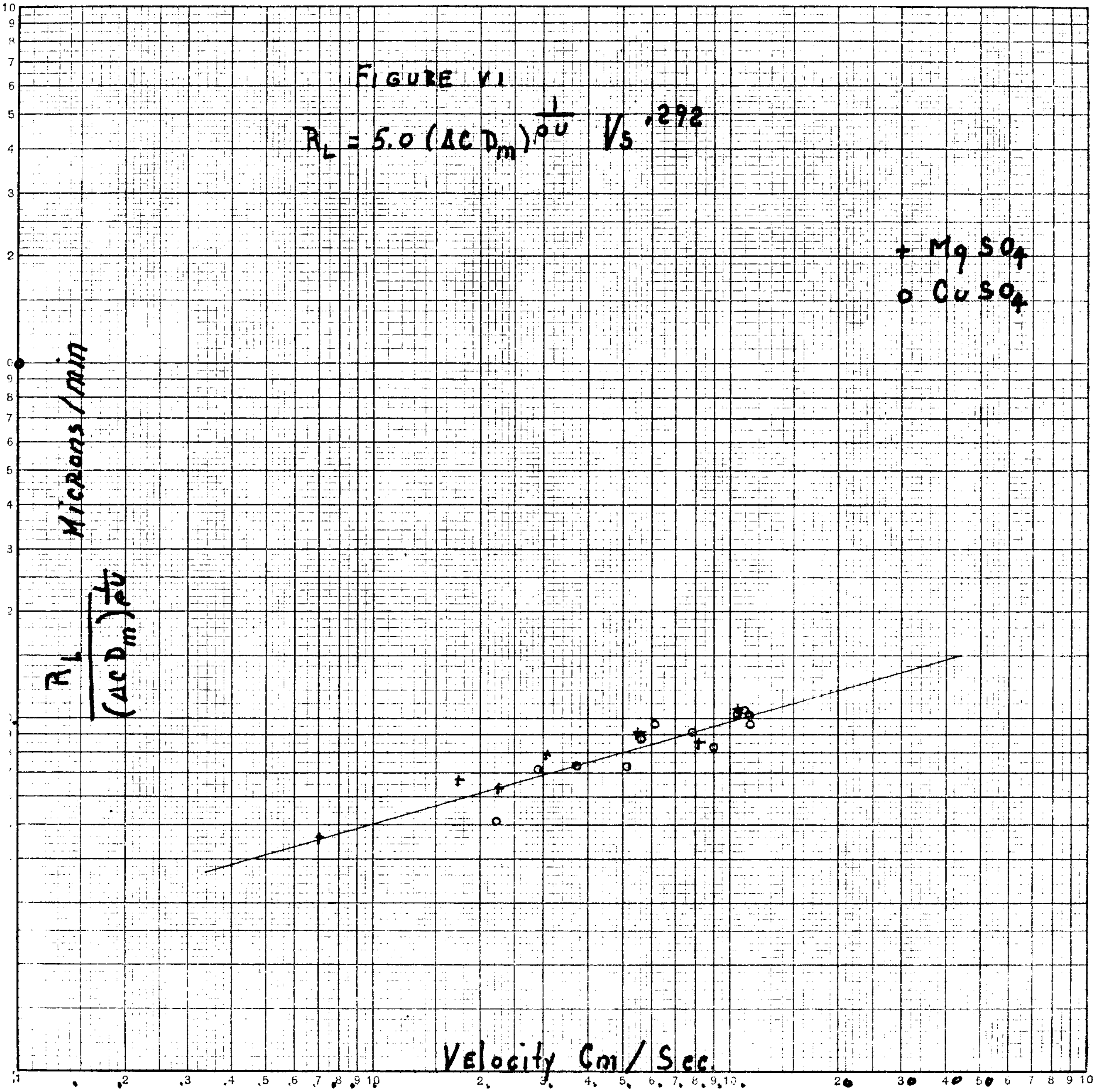


FIGURE VI

$R_L = 5.0 (\Delta C D_m)^{\frac{1}{\rho u}} V_S^{.292}$

CONCLUSION

Figure III indicates that the McCabe and Stevens (2) data is quantitatively less than that of the author; and in reviewing the article by McCabe and Stevens (2), two points are brought forth as evidence as to the invalidity of their data:

One: Only 400 c.c. of solution were used for a series of runs, thus giving a diminishing concentration rate. Temperature was held constant, and since the solution was not allowed to return to a saturator to obtain its equilibrium conditions with regard to concentration, it would therefore give results lower than that of the author.

Two: McCabe and Stevens' (2) velocities were determined by a stirrer speed in a U-tube. The author measured velocity by weight and computed velocity in terms of cm/sec. It is therefore questionable as to the correct velocity being obtained by McCabe and Stevens (2) of solution past the crystal.

Results of the author's investigation indicate the following:

(1) that crystal size has no effect on crystal growth.

(2) that velocity within the range studied is the rate determining factor.

Conclusion (Continued)

(3) that the rate of growth is less at lower velocities than at higher velocities.

(4) that through the use of the diffusivity data, viscosity, density and velocity of solution past the crystal, it is possible to obtain a correlation for pure crystal growth systems. The data on diffusivity is limited and the author feels certain that as time and technology progress, data of more salts will be available for correlation with greater accuracy obtainable with regard to crystal growth.

The equation derived is as follows:

$$R_L = 5.0 \left(\Delta C D_m \right) \frac{1}{\rho \nu} V_s^{.292}$$

This equation satisfies the requirements as shown in Figure VI.

(5) McCabe and Stevens (2) assumed viscosity and density constant in their equations. The author incorporated these constants, i.e. at 27°C temperature, in the above equation in order to obtain a correlation for the rate of crystal growth of copper sulfate and magnesium sulfate crystals.

RECOMMENDATIONS FOR FUTURE STUDY

Since the study of crystal growth, no one has, to the writer's knowledge with reference to solution velocity, used a seed crystal of the exact crystal lattice of the type of crystal being studied. It is therefore recommended that a seed crystal be grown in the following manner:

Drill a fine hole into the crystal and insert a piece of stainless steel wire slightly larger in diameter than that of the drilled hole. By wetting the wire it should slip in and upon evaporation of the water, the wire will become fused to the crystal. The crystal should then be placed in a saturated solution and allowed to grow until a good-shaped crystal is formed, namely, one that can visually with the eye be micrometered. This will give seed crystals which will not need a holder for suspension in the solutions.

The equipment should be entirely closed with proper facilities for opening the solution chambers. It should also be designed with a minimum of three test sections so that more data can be obtained per run.

A weighing vessel should be installed on the discharge side of the test section, just prior to the saturator. This would run with a by-pass so that periodically a three-way valve can be changed to give weight determinations.

Recommendations for Future Study (Continued)

There should be a drain valve to allow drainage back to the saturator.

A rotometer should be installed, but only as a convenience so as to quickly set a flow rate; but again velocity determination should be by weight alone.

The pump should be of a positive displacement type with a variable speed drive. It should be properly bypassed and have a pneumatic control valve to take up any fluctuation with reference to pump imperfections.

The writer feels that a true velocity past the crystal being grown has not been done even though a closer attempt was made in this work.

A means of automatically heating the saturator to saturation temperature prior to the arrival of the worker would be a great asset in making more runs per day.

By measuring the crystal with a micrometer or vernier, crystal faces can be oriented and size changes noted.

APPENDIX

TABLE VI

International Critical Tables

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$CuSO_4 \cdot 5H_2O$ -

Temp. °C	Solubility Gms/100 gms free H_2O
10	26.9
20	32.4
25	35.5
30	38.1
40	44.9
50	52.2
56	The A and B are present

$MgSO_4 \cdot 7H_2O$ - Vol. IV - Page 228

10	62.5
20	70.6
30	81.5
40	91.4
48.2	The heptahydrate and hexahydrate are present.

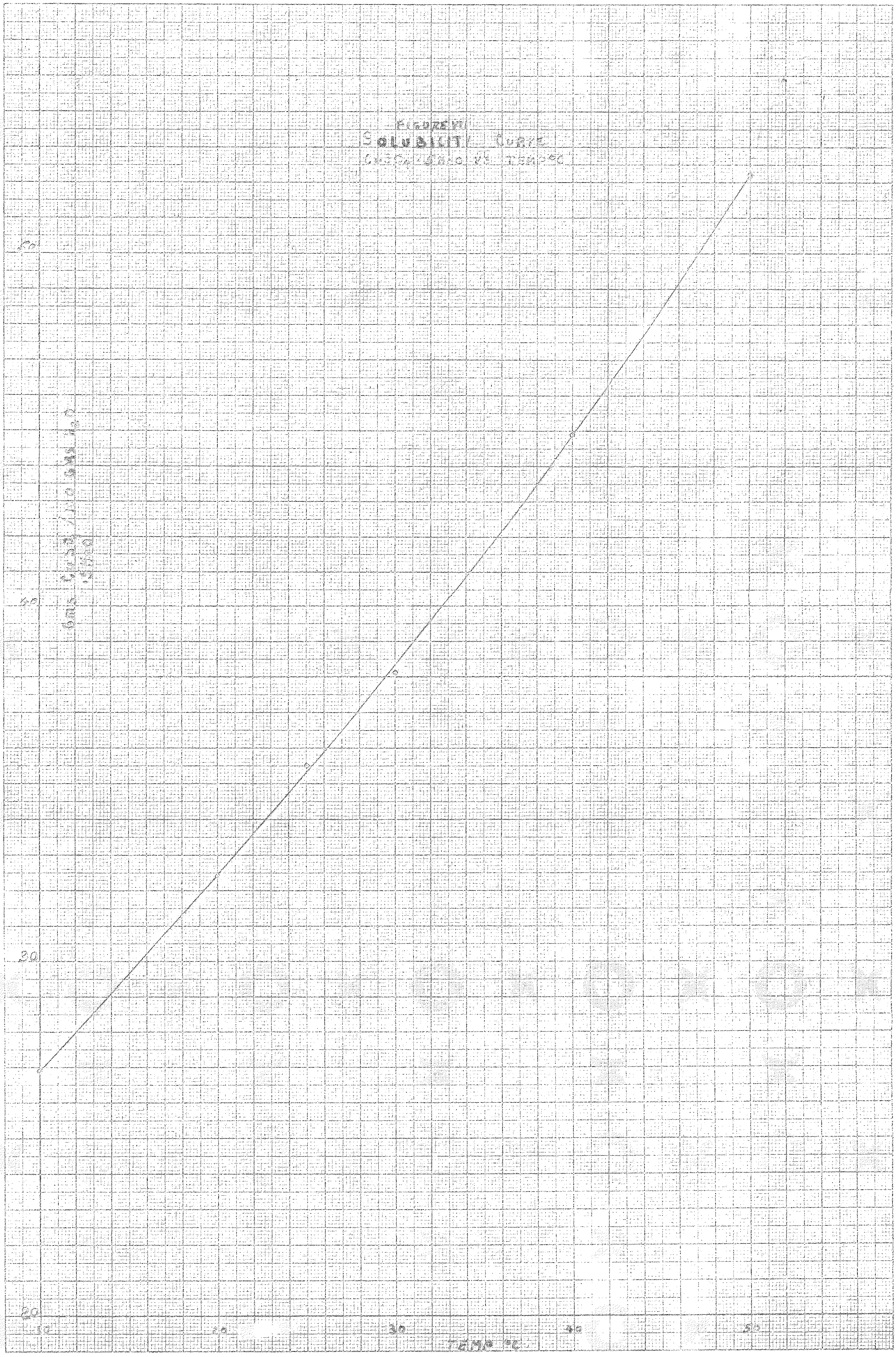


FIGURE VII
SOLUBILITY CURVE
$CuSO_4 \cdot 5H_2O$ vs TEMP °C

FIGURE VIII

SOLUBILITY CURVE

$MgSO_4 \cdot 7H_2O$ Vs Temp °C

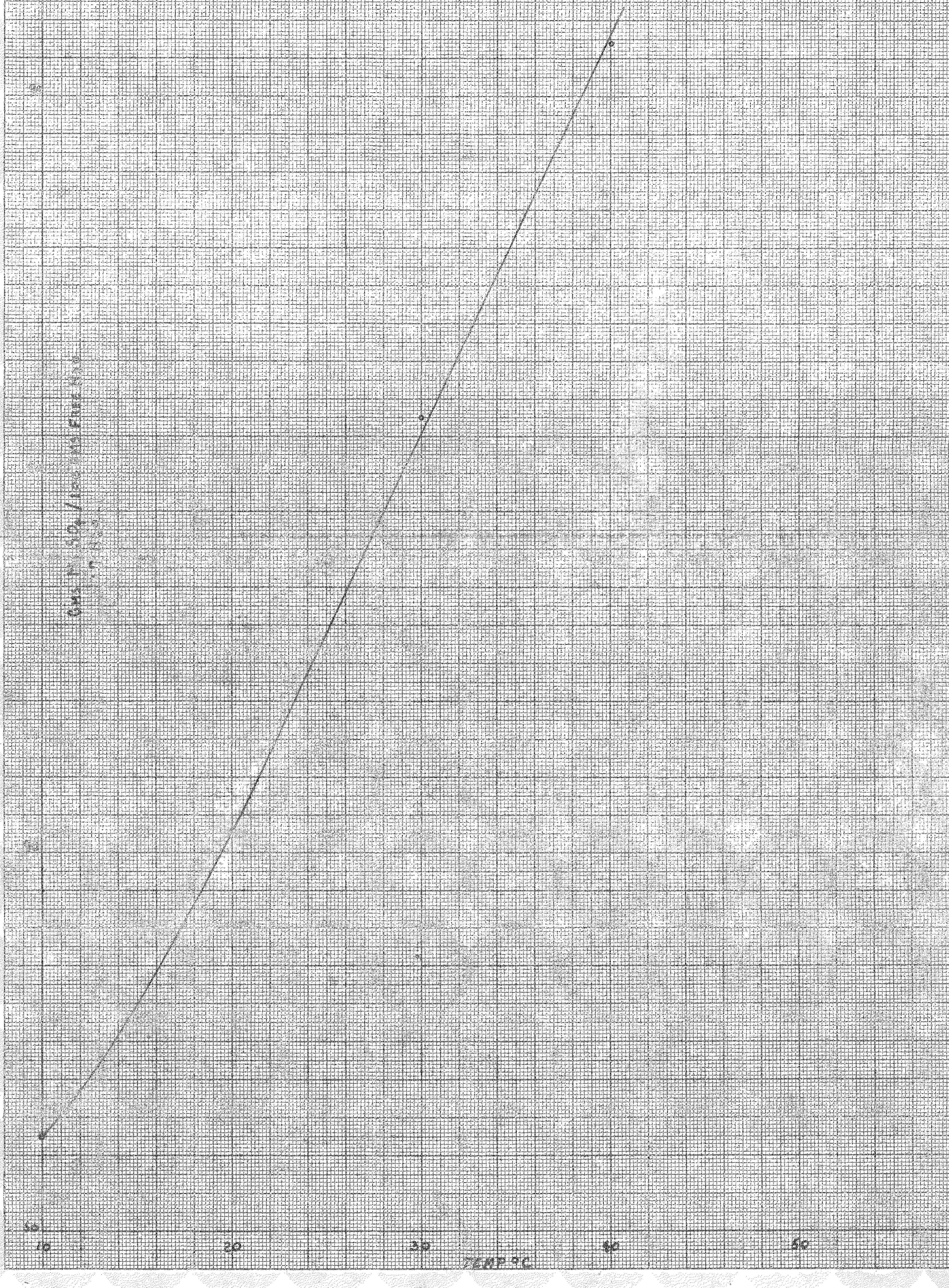


TABLE VII

This table obtained from Hixson and Knox (1) who in turn extrapolated from the data of Oholm (10).

Values of the Viscosity, Density, and Diffusivity of Saturated Copper Sulfate Solutions

Temp. °C	Viscosity C/P	Density Gram/Ml.	Diffusivity (a) $D_m \frac{\text{Lb. Moles}}{\text{(Hour)(Foot)}}$
19.3	2.21 (b)	1.20 (c)	4.7×10^{-5}
41.4	1.97	1.27	7.4×10^{-5}
53.5	1.92	1.31	9.0×10^{-5}
71.2	1.94	1.41	12.3×10^{-5}

(a) Extrapolated from the data of Oholm (10)

(b) From the International Critical Tables (4)

(c) From the data of Flottmann (1)

FIGURE IX

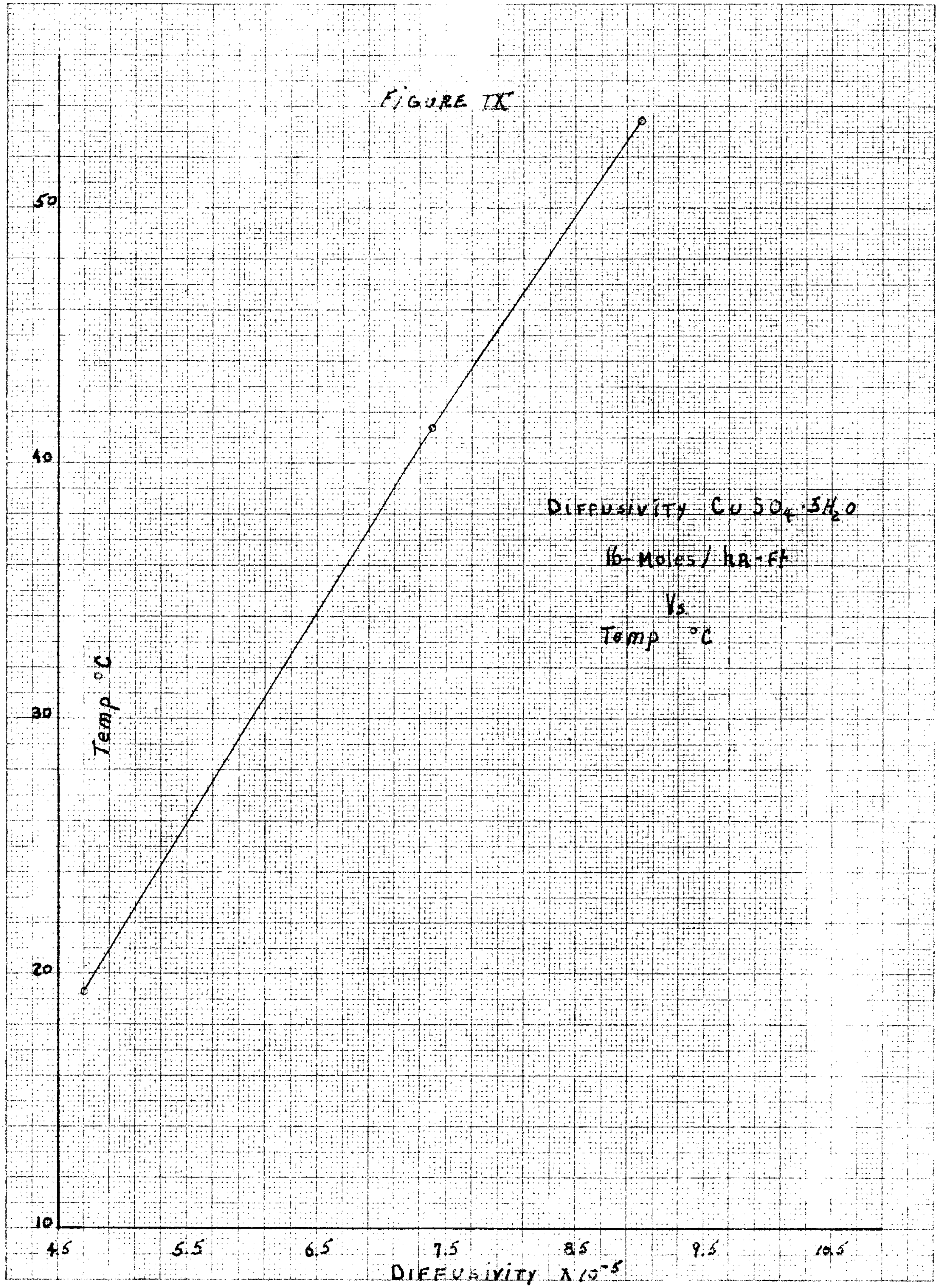
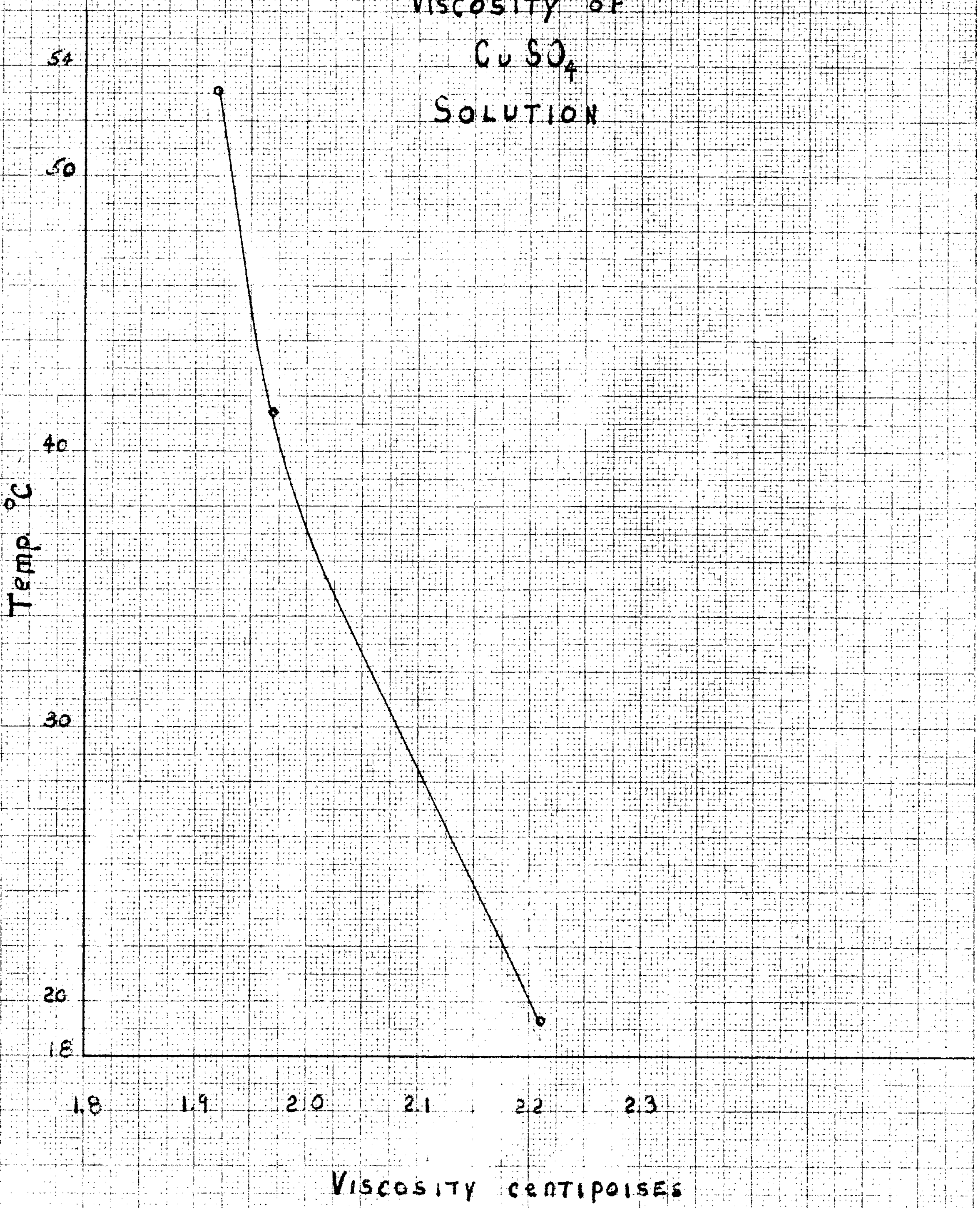

DIFFUSIVITY $CuSO_4 \cdot 5H_2O$
lb-Moles/hr-ft
Vs.
Temp °C
Temp °C
50
40
30
20
10
4.5
5.5
6.5
7.5
8.5
9.5
10.5
DIFFUSIVITY $\times 10^{-5}$

FIGURE XII

VISCOSITY OF $CuSO_4$ SOLUTION



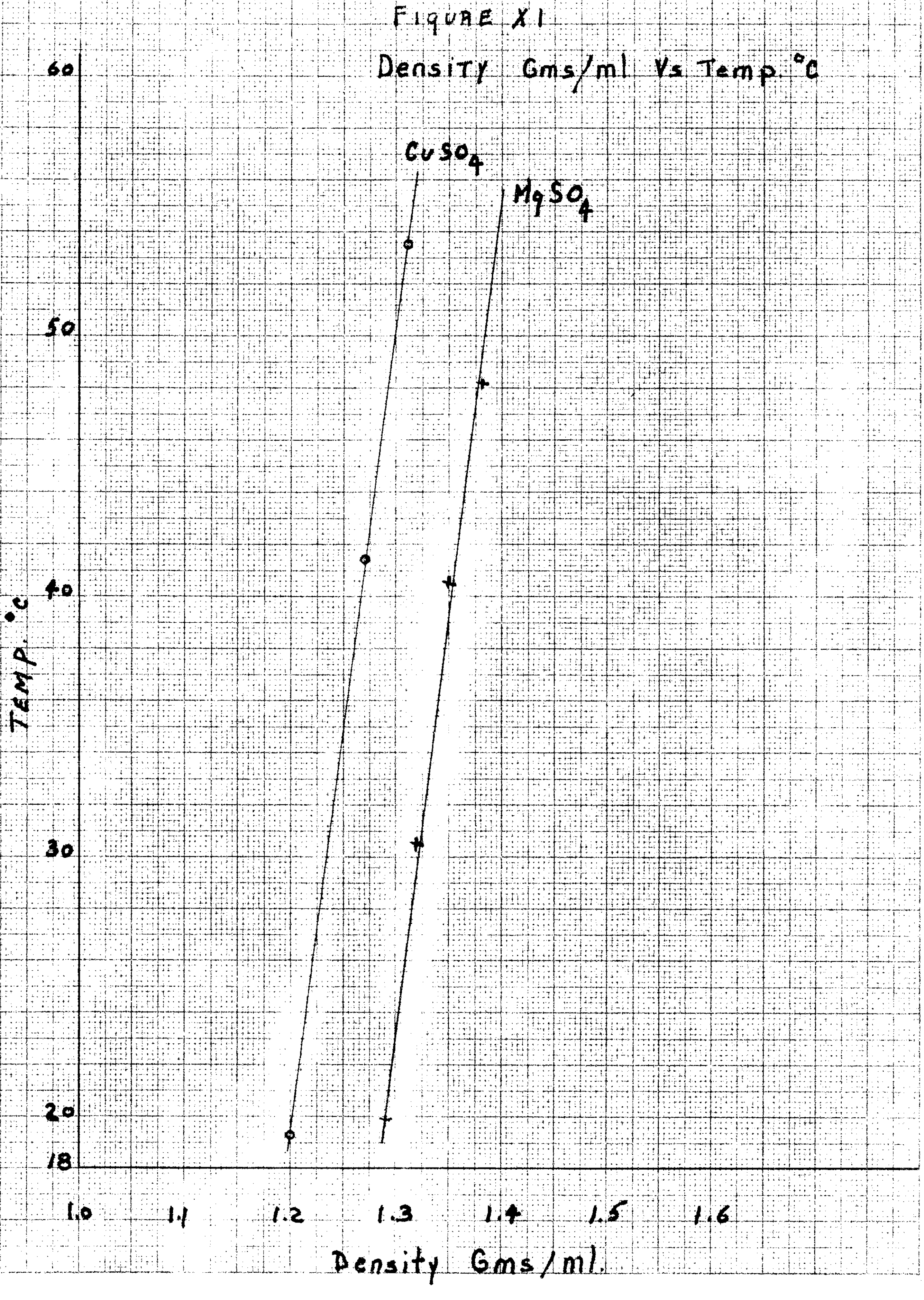


FIGURE XI

Density Gms/ml Vs Temp. °C

TABLE VIII

This table obtained from Hixson and Knox (1) who in turn extrapolated from the data of Oholm (10).

Values of the Viscosity, Density, & Diffusivity of Saturated Magnesium Sulfate Solutions

Temp. °C	Viscosity C/P	Density Gram/Ml	Diffusivity (a) D_m $\frac{\text{Lb. Moles}}{\text{(Hour)(Foot)}}$
19.9	6.8(b)	1.29(b)	3.18×10^{-4}
30.5	7.66	1.32	3.56×10^{-4}
40.5	8.15	1.35	3.92×10^{-4}
48.2	8.50	1.38	4.02×10^{-4}

(a) Extrapolated from the data of Oholm (10)

(b) From the International Critical Tables (4)

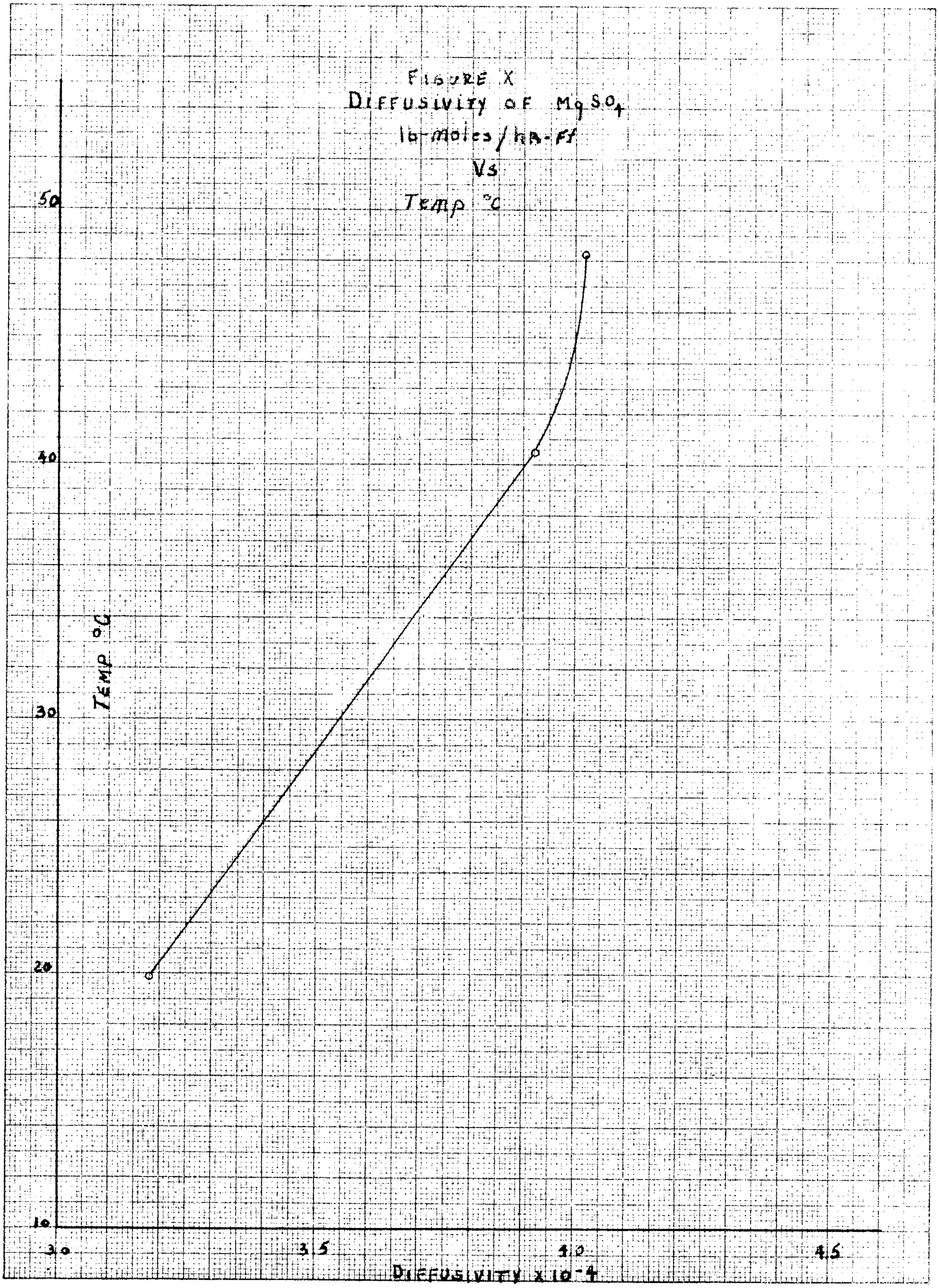
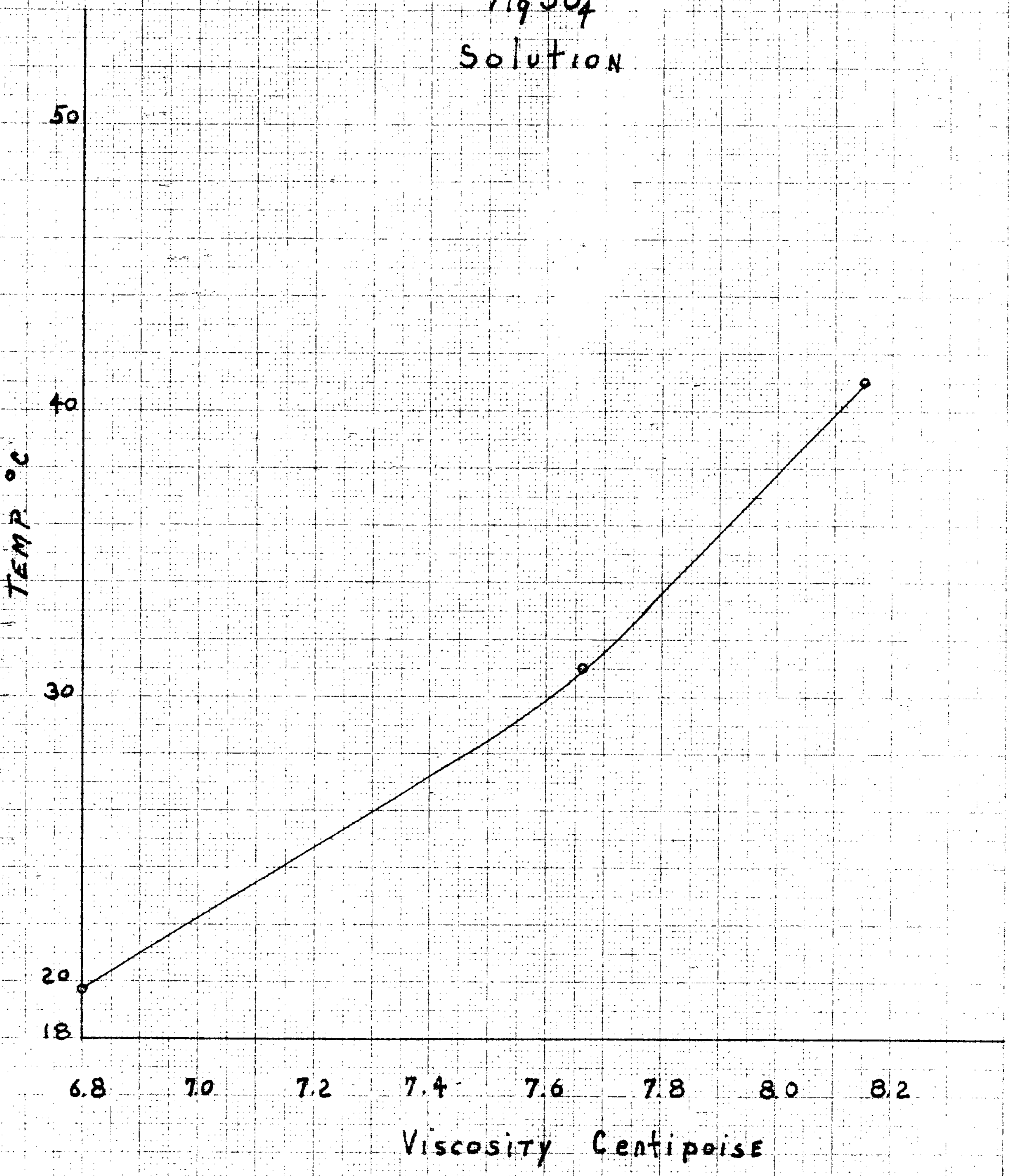


FIGURE X
DIFFUSIVITY OF $MgSO_4$
lb-moles/hr-ft
vs
Temp °C

FIGURE XIII

Viscosity of $MgSO_4$ Solution



NOTATION

R_L = growth rate microns/min.

S_1 = crystal size before growth.

S_2 = crystal size after growth.

V_s = solution velocity.

C = Concentration gms salt/100 gms free water.

T_s = temperature of saturated solution °C.

T_{ss} = temperature of supersaturated solution °C.

D_m = diffusivity constant

ρ = density of solution

U = viscosity

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