LINEAR GROWTH RATES OF SINGLE

COPPER SULFATE CRYSTALS

BY

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POLYTECHNIC INSTITUTE OF BROOKLYN, 1950

SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

IN CHEMICAL ENGINEERING

IN THE

GRADUATE DIVISION

AT THE

NEWARK COLLEGE OF ENGINEERING

1954

SIGNATURE OF AUTHOR ______________________

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APPROVAL SHEET

APPROVED BY

ACKNOWLEDGEMENT

The writer gratefully acknowledges the counsel and advice of Executive Associate George Keeffe throughout the course of this thesis; and the permission of Mr. T.J. Sullivan for use of the crystal apparatus in this work.

ABSTRACT

The purpose of this work was to study and measure the factors influencing crystal growth.

Approximately 250 single crystals of $CuSO_4 \cdot 5H_2O$ were grown under controlled conditions of supersaturation, solution velocity, and temperature.

The data from this work indicates that:

(a) Crystal growth rate is independent of crystal size for the size range covered (4 to 12 mesh).

(b) Crystal growth rate is directly proportional to the degree of supersaturation, or driving force for each concentration of solution studied.

(c) Crystal growth rate varies exponentially with the velocity of the solution passing the crystal

$$R_D = f(u^m)$$

(d) The value of the exponent "m" increases as the temperature (and concentration) of the growth solution increases. This indicates that there must be more than one dimensionless group containing the velocity term.

The following empirical equations were obtained for the four different solutions used:

Solution A - Saturation temperature = 28° C.

$$\log \frac{R_D}{\Delta C} = 0.240 \log u + 0.2900$$

Solution B - Saturation temperature = 37° C.

$$\log \frac{R_D}{\Delta C} = 0.265 \log u + 0.5682$$

Solution C - Saturation temperature = 47° C.

$$\log \frac{R_D}{\Delta C} = 0.288 \log u + 0.6128$$

Solution D - Saturation temperature = 58° C.

$$\log \frac{R_D}{\Delta C} = 0.407 \log u + 0.6721$$

(e) The following empirical equation was derived which composites the above equations and which effectively summarizes all the data in this work:

$$R_D = 30{,}000 \, \Delta C \, u^2 \, e^{\frac{-2950 \, u^{.143}}{T}}$$

The velocity range in this work was from 2.2 to 20.6 centimeters per second.

INTRODUCTION

Although crystallization continues to be one of the most important unit operations, little is known of the mechanism by which crystal growth takes place.

To obtain such knowledge, many growth studies of single crystals are necessary. It is generally understood that the two prime factors governing growth rates are the diffusional or physical process, and the chemical or ionic orientation reaction. Undoubtedly the relative importance of these factors vary with each crystalline substance.

It is believed that the growth process is an intermittent one, and not continuous. A definite activation energy is required to form a "unit" or "step" on a crystal surface, after which a layer of definite thickness rapidly "fills up" the remaining available crystal area. This concept explains many growth phenomena such as:

(a) retention of geometric shape

(b) strained growth under forced conditions

(c) "twinning" - this writer accounts for such a phenomena by visualizing two crystals colliding face to face at the instant a layer is being formed.

(d) growth of crystals in this work, wherein one side of a crystal is exposed to the full force of solution flow.

This study of the unit operation of crystallization was made to confirm and supplement the past work of McCabe and Knox. This writer has attempted to obtain data, correlate the effects of the prime variables, and develop empirical relationships in an original manner. Use of equipment and utilities was permitted by the Supervisor of the Research Department of the American Agricultural Chemical Co. at Carteret, N.J., for increased understanding of crystallization problems.

In conducting this study, and apparatus was used which composites many features used by perhaps a dozen different investigators. The following minor objectives were kept in mind in order to obtain the final correlations:

1. Simultaneous growth of several different size crystals under identical conditions of supersaturation, velocity, and concentration.

2. Obtain a greater degree of supersaturation than that obtained by previous investigators.

3. Ascertain the quantitative effect of supersaturation under conditions of constant velocity.

4. Simultaneously grow single crystals under variable velocity but constant supersaturation conditions. This was not attempted by previous investigators.

5. Devise a simple, precise method for measuring solution concentration.

6. Obtain solubility data for the copper sulphate-water system of greater accuracy than data in the International Critical Tables and Seidell's "Solubility of Inorganic Compounds". Solubility data from these two references do not agree.

It is believed that this paper is the first to present the fact that solution velocity (agitation) exerts greater influence on a crystal growth process at high temperatures than at low temperatures. This is confirmed by a study of the data of Hixson-Knox.

This paper is the first to indicate that the growth rate of copper sulphate is directly proportional to the degree of supersaturation.

This is confirmed by a study of the data of Hixson-Knox.

REVIEW OF LITERATURE ON CRYSTAL GROWTH

References

(9) Curie 1885 - "Each face of a crystal has a capillary constant which controls growth rate".

(9) Wulff 1901 - This writer measured velocities of growth of ferrous alum and found that every face had its own rate of extension measured normally to surface. He assumed the capillary constants were proportional to the rates of growth of the various faces.

(9) Noyes-Whitney - dissolution theory

$$\frac{dW}{dt} = -R_D = k\bar{A}\,(\Delta C)$$

(8) Noyes-Whitney - rotated sticks of benzoic acid and $PbCl_2$ in fresh water at constant velocity and constant temperature. The following relation was obtained:

$$kt = \ln\left[\frac{C_s - C_0}{C_s - C}\right]$$

(8) Mars R. 1908 - found certain salts whose rate of crystallization was independent of stirrer speed.

(9) Mars R. 1912 - "For many substances at low rates of growth and low supersaturation growth is a bimolecular or second-order reaction. As supersaturation increased the growth approached a first-order reaction".

(9) LeBlanc-Schmant - Studied several salts and found value of K in Noyes-Whitney equation to be different for growth and dissolution.

(9) Nernst - Modified Noyes-Whitney equation.

$$\frac{dx}{dt} = \frac{DA}{\delta} \times \Delta C$$

(9) Berthand - Stated that solution at surface of growing crystal was not saturated but was slightly supersaturated - growth occurs in pulses, is discontinuous.

(a) first order reaction:

$$\frac{dx}{dt} = k_1 A\,[C_i - C_0]$$

(b) then stationary state - diffusion takes place

$$\frac{dx}{dt} = \frac{D\bar{A}}{\delta}\,[c_B - c_i]$$

References

(c) combining above equations:

$$\frac{1}{A}\frac{\partial x}{\partial t} = \frac{D}{\delta + D/k}(c_B - c_o) = R(\Delta c)$$

(9) Wenk, W. (pupil of Marc) - Experiments with potassium sulfate.

$$\frac{\partial p}{\partial t} = k(c_B - c_o)^2$$

(10) Campbell, H.P. 1915 - The author suspended single potassium alum crystals in a slightly supersaturated, agitated solution. Obtained the relationship:

$$m^{1/3} = kt$$

(2) Wilhelm, Conklin & Sauer (1941) - The rate of solution of sodium chloride crystals was studied - the following equation was obtained:

$$-\frac{\partial w}{\partial t} = \frac{D}{\delta}A(c_s - c_B) = kA(\Delta c)$$

$\frac{\partial w}{\partial t}$ = mass transfer rate

A = area of particles

D = specific diffusivity

δ = effective film thickness

k = diffusion rate constant

(3) Hixson, A.W. 1944 - Author described the effect of agitator speed on velocity of heterogenous reactions.

$$K = \alpha N^{\beta}$$

where: K = reaction velocity constant

N = rpm of stirrer

α, β = constants

(a) When a reaction is diffusion controlled $\beta \cong 1$.

(b) When reaction is controlled by the rate of interfacial reaction, $\beta \to 0$

(4) Van Hook 1944 - This writer added measured quantity of 40-60 mesh sucrose seeds to an agitated vessel containing supersaturated sugar syrup. He repeated this experiment with syrups of different saturations and obtained the following correlations:

$$-\frac{\partial c}{\partial t} = k(c - c_{\infty})$$

where $k = \frac{1}{t}\log\frac{m_o - m_{\infty}}{m - m_{\infty}}$

References

C = weigh fraction sucrose in syrup

C_∞ = fraction in saturated syrup

n_0 = refractive index of initial syrup

n = final refractive index of syrup

n_∞ = index of saturated syrup

t = time

(5) Van Hook 1944 - Found that increasing viscosity of sugar syrups did not effect crystallization rate. Viscosity was increased by addition of gum acacia and starch.

(6) Hixon and Knox - 1951 - These authors collected voluminous data on the growth of single crystals of copper sulfate and magnesium sulfate. The authors were able to correlate their data in the following manner:

(a) Diffusion - mass transfer

$$\left[\frac{F_D D_E}{D_m}\right] = C\left[\frac{D_e V \rho}{\mu}\right]^d \left[\frac{\mu}{M_m D_m}\right]^e$$

(b) Surface reaction

$$w_a = F_R (y_F - y_i)^\alpha ; \quad \ln F_R = \frac{E}{RT} + b$$

(c) Diffusion - heat transfer

The authors considered this to be of negligible effect in the systems studied.

(7) W.L. McCabe - R.P. Stevens - 1951 - Seed crystals of copper sulphate were introduced into a supersaturated solution which was agitated in a conventional vessel. Rate of growth was correlated with crystal size and degree of supersaturation:

$$r_g = 0.00177\, L^{1.1}\, \Delta C^{1.8}$$

It was thought that the crystal size was not a prime variable, but rather an apparent one since the relative velocity between solution and crystals increases as the crystal size increases under normal mixing conditions.

References

Seed crystals were then enclosed in a perforated cage which was suspended in a flowing stream of solution. Experiments were also carried out in a reciprocating cage.

General correlation:

$$\frac{1}{r_g} = \frac{1}{r_0 + \beta u} + \frac{1}{r_i}$$

r_g = growth rate - μ/min
r_0 = growth rate at zero velocity
β = constant
u = velocity - cm/sec.
r_i = interfacial growth rate

V. Description of Apparatus

The apparatus used for the bulk of this work consists of the following:

(1) Crystallizer Tube - A pyrex glass tube 1-7/8 inches in diameter and about three feet high. The tube is provided with a tapered bottom and three outlets.

(2) Crystal Basket - A basket constructed of 15 mesh copper screen was used to support 3 or 4 single crystals. The basket is supported in the crystallizer tube by means of a copper wire attached to a rubber stopper.

(3) Thermometer (accurate) - Temperature of the solution flowing past the growing crystal measured by a 0-110°C. thermometer (divisions 0.1°C.).

(4) Dissolver - A four liter Pyrex beaker.

(5) Heater - An electric heater designed for submersion in corrosive liquids. This heater is constructed of stainless steel and provided with 3 settings (low, medium, high) for variable heat output. This writer fitted the heat output adjustment knob with a numerical scale (reading 0-10) for better control of heat output. The heater is manufactured by the Stillman Co., N.Y.C. under the trade name "Chill Chaser".

(6) Recycle Pump - A stainless steel centrifugal pump used for circulating the copper sulphate solution.

(7) Thermometer (ordinary) - An ordinary 0-110°C. mercury thermometer.

(8) Cooler - an ordinary laboratory condenser provided with inlet and outlet for cooling water.

(8A) Cooler - a copper coil five feet long and 1/4 inch diameter used in place of the glass cooler (8) to obtain greater cooling capacity.

(9) Small cool water tank - a two liter beaker provided with a bottom outlet.

(10) Cool water pump - same type pump as (6) used for circulating cooling water.

(11) Large cool water tank - An eight gallon iron bucket used for storing cooling water.

(12) Brass crystallizing tubes - three brass pipes (1", 3/4", 1/2" IPS) connected in series with or without the glass crystallizer tube to obtain 3 or 4 solution velocities.

(13) Control Panel - Consists of two dial-rheostats (scale reading 0-100) for controlling flow rates of copper sulphate solution and cooling water.

VII. General Procedure

A solution of predetermined concentration of copper sulphate is introduced into the crystallization apparatus. By preheating the solution 10-15° C. above the saturation temperature, crystallization, or freeze up in the apparatus is avoided.

The solution pump is then started to circulate the solution around the apparatus. The cooling system is then placed in operation to bring the solution down to the saturation temperature. As the saturation temperature is approached, the electric submerged heater is turned on. To maintain a stable system, the solution temperature in the dissolver is kept above saturation. By controlling the degree of heat input plus heat removal from the system, any desired supersaturation can be maintained in the crystallizer tube.

The solution is then sampled for a check on the concentration by taking a hot Baume measurement (see Detailed Procedure).

Three or four different size crystals (6 to 12 mesh) are then individually weighed and placed in a copper wire basket, which in turn is suspended in the top of the crystallizer tube. The time is then noted.

A record of the crystallizer temperature is kept throughout the run.

After the growth period (from 20 to 120 minutes depending upon growth rate) the crystals are removed and weighed.

The cooling and heating adjustments are then changed in preparation for the next run.

Care is taken to insure that the temperature in the dissolver is above the saturation temperature. Otherwise, the solution will "break" and freeze up the entire apparatus. When this occurs, the tedious operation of dissembling, cleaning and reassembly of the entire apparatus is often necessary.

With most of the growth experiments, the solution was raised 5-10° C. above the saturation temperature for 15-30 minutes between each run. This dissolved any small crystals (rarely present) in the cooler or the line leading to the crystallizer.

From 3 to 8 experiments (runs) were made in a series. Fresh solutions were made up for each series. Dust particles and insoluble matter were removed by filtering through Super-Cel.

IV. Sequence of Study

Potassium alum was the material first selected for study since large crystals of this substance may be grown with comparative ease. Considerable experimental time was devoted to the simultaneous growth of single crystals and a fluidized crystal bed. The single crystals were permitted to grow suspended in a wire basket at the top of a crystallizer tube. A moving bed of crystals at the lower tapered end of the crystallizer tube was permitted to grow at the same time under identical conditions of concentration and temperature.

After four such experiments the system for study was changed to $CuSO_4 \cdot 5H_2O$ because of the greater availability of physical data such as viscosity, density, etc. Furthermore, it was desired to check the data with that of McCabe (1) and Hixson (2).

Experiments number 5, 7, and 8 were conducted to simultaneously measure growth rates of single crystals and a fluidized bed as was previously done with alum.

The rest of the experiments were concerned with the growth of single crystals only for reasons later taken up in the discussion.

Runs 5, 6, 7, 8, were designated as Series I, and the results were found to be of a magnitude similar to that reported by McCabe (1), for solutions at 28° C.

For the second series a solution concentration of 63 grams $CuSO_4 \cdot 5H_2O$ per 100 grams of free water (C_B = 63) was prepared (saturation temperature about 47° C). For this series, velocity was kept constant and ΔC was varied.

A copper cooling tube was substituted for the glass cooling condenser prior to Series III.

Series III was also carried out at about 47° C., at constant velocity, and under conditions of variable supersaturation (ΔC).

For Series IV and V, the glass crystallizer tube was replaced by three brass tubes (1" IPS, 3/4" IPS, 1/2" IPS) connected in series. Crystals were grown in each of these tubes in order to ascertain the effect of velocity on growth rate. A velocity range of 2.8, 7.0, 11.5, and 20.6 cm per second was thus obtained. With the glass crystallizer tube, the velocity range was limited by the output of the pump.

Series VI was conducted to check Series III. Series III, IV, V, and VI, were done using about the same concentration of solution (C_B = 63, T_S = 47° C).

Series VII was done at one velocity using a weaker solution (C_B = 53, T_S = 37° C.)

The eighth series was conducted using the three brass tubes and a solution having same concentration as Series VII.

To cover further the study of the concentration and velocity variable, series IX and X were carried out using solutions (C_B = 44, T_S = 27° C.) and (C_B = 78, T_S = 58° C.). The effect of four different solution velocities was obtained by connecting the glass crystallizer tube and the three brass tubes in series.

DETAILED PROCEDURE

MEASUREMENT OF SOLUTION CONCENTRATION

The copper sulphate used in this work was of a technical grade:

Brand Name:	Nichols Triangle Brand
Producer:	Phelps Dodge
Copper:	25.2% Cu Minimum
Blue Vitriol:	99% Minimum
Insolubles:	1% Maximum

Method

1. A weighed amount (40-150 gm) of crystals in a 400 cc beaker is dissolved by heating with approximately 300 cc of water. The temperature of the solution is then brought to 63° C.

   The well-mixed solution is then quickly weighed and transferred to a hydrometer cylinder. A standardized hydrometer is then inserted and a reading rapidly taken. The temperature is then noted (invariably 60° C ± 0.3°)

Data	Gms BV	Gms Soln	% AV	Be 60
	90.0	305.5	29.4	24.2
	105.0	298.1	35.2	29.0
	120.1	301.8	39.8	32.7
	135.0	304.4	44.3	36.7
	150.0	440.4	34.08	28.1
	90.1	369.6	24.4	20.05
	45.2	364.2	12.4	9.4

2. The data was then plotted on a large sheet of graph paper (rectangular coordinates). The seven points were found to lie on a straight line which when extended gave a negative baume value (-2.2° Be) at zero percent $CuSO_4 \cdot 5H_2O$. This was expected since the plot was based on a temperature of 60° C.

3. About 25 points were then picked from the plot and recalculated. Weight percent was converted to Grams $CuSO_4 \cdot 5H_2O$ per 100 gms. of free water.

4. The 25 values were then replotted as gms $CuSO_4 \cdot 5H_2O$ per 100 gm. of free water vs. Be 60° C. (Figure I)

Concentration data for this work (C_B) was obtained from Baume data by the use of this plot. Some skill and reasonable speed is required for taking the baume data, otherwise surface evaporation will change the concentration.

DETAILED PROCEDURE - SOLUBILITY DATA

1. Set up apparatus as shown on Figure C.

2. Add copper sulfate solution and a large excess of 20 mesh crystals to the inner beaker so that the liquid level is even with that of the outer water bath.

3. Turn on both agitators and bring the temperature of the water bath to about 1/2° C. above desired temperature in inner vessel. Maintain constant temperature of outer bath.

4. When the temperature in the inner beaker reaches a constant value, note the time and temperature.

5. Maintain temperature of inner and outer fluids to the nearest 0.1° C. for 1/2 hour.

6. Stop inner agitator, allow 15 seconds for any crystal fines to settle, and quickly draw a solution sample. Obtain baume value by method previously described.

7. Start inner agitator, and obtain a check baume value on a second sample after 15 minutes.

8. Obtain baume data in this manner at four other saturation temperatures. Plot a smooth curve of baume versus T_S to verify data.

9. Convert baume data and plot concentration versus saturation temperature on figure I .

DETAILED PROCEDURE

MEASUREMENT OF CRYSTAL GROWTH

1. Select and weigh a clear, well formed crystal to 0.0001 gram.
2. Transfer with rubber forceps to previously cleaned and dried copper basket.
3. Suspend basket in crystallizer tube when temperature is constant. Note time.
4. After growth period, remove basket and place on a blotter paper.
5. Immediately dip basket and crystal two or three times in 90% methanol.
6. Place basket on another blotter paper.
7. Dump crystal onto a sheet of dry filter paper and allow to dry for ten minutes.
8. Weigh crystal - discard, or use for following run.

CALCULATION - crystal geometry

During the course of this work, it was noted that the crystals were not all of the same shape. Some of the crystals were elongated and others were stubby. In general, the crystals grown for this work had the same shape and were visually selected from a previously prepared quantity of crystals.

For simplicity of presentation and evaluation of data, this writer has defined the growth rate, R_D, as follows:

$$R_D = 1{,}120 \left[\frac{W_2^{1/3} - W_1^{1/3}}{\theta} \right]$$

where: R_D = linear growth rate - microns per minute

W_2 = final weight of crystal - mgm

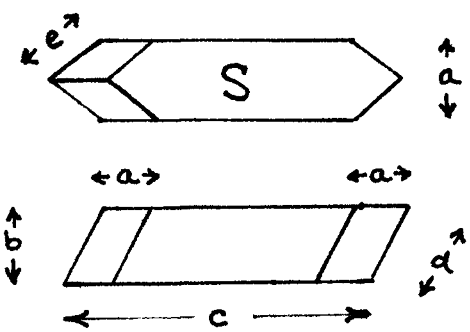
W_1 = initial weight of crystal - mgm

θ = growth time - minutes

The constant (1,120) was obtained by calculation on the basis of an observed crystal shape and the value of the crystal density from Lange's Handbook (ρ = 2.286 gm/cc)

- Observed average crystal dimensions - relative

- assume two of the axis perpendicular



a:b:c:d:e: = 1:1.5:4.0:1.7:1.1

(1) Area S = $\frac{a^2}{2} + 2a^2 + \frac{a^2}{2} = 3a^2$

(2) Crystal volume = $S \times b = 3a^2 b = \underline{4.5\,a^3}$

(3) Crystal area $= 2[2ab + 2bc] + 2(3a^2)$

$= 4[1.5a^2 + (1.5a)(1.1a)] + 6a^2$

$= \underline{18.6\,a^2}$

Crystal weight (mgm) = $\rho \frac{mgm}{mm^3} \times V\ mm^3$

$$W = \rho V = 2.286 \times 4.5\,a^3$$

$$\underline{a = 0.460\,W^{1/3}}$$

(1) Sphericity - The size of an irregular particle may be expressed as the diameter of a sphere having the same surface area as the particle. (used by Hixson)

$$A = 18.6\ a^2 = \pi D^2$$

$$D = 2.43\,a = 2.43\ (.460\ w^{1/3}) = 1.120\ w^{1/3}$$

$$R_D = \frac{\Delta D}{\theta} = \left[\frac{\Delta w^{1/3}}{\theta} \times 1.120\right] \frac{mm}{min}$$

$$R_D \frac{\mu}{min} = 1{,}120\ \frac{\Delta w^{1/3}}{\theta}$$

(2) McCabe Method - The size of the crystal is expressed as the square root of the product of the longest and shortest dimension.

$$L = \sqrt{ac} = 2a$$

$$L = 2\,(.460\ w^{1/3}) = .920\ w^{1/3}\ \frac{mm}{min.}$$

$$R_L = 920\ \frac{\Delta w^{1/3}}{\theta} = \frac{\mu}{min}$$

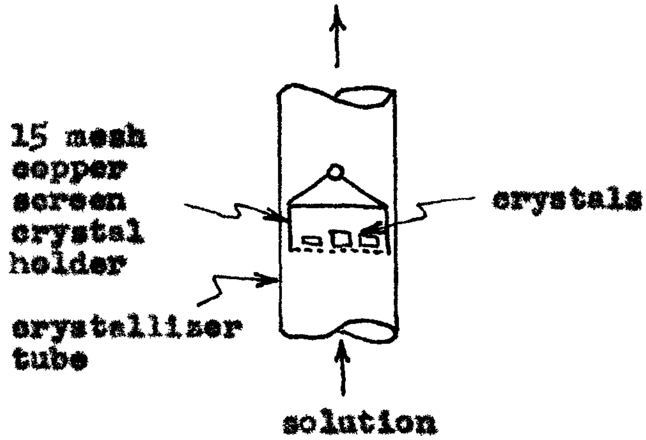
$$R_D = 1.22\ R_L$$

CALCULATION - Velocity

FLOW AREA CORRECTION - Copper Basket

Basis: 1 sq.in. (= 6.45 cm^2)

Wire diameter = 0.0286 cm.



Area of wire interrupting flow (per square inch) $= 30\ (2.54\ \frac{cm}{in}) \times .0286 - 15^2 (0286)^2$

" $= 2.00$

% area of wire = 2.00/6.45 = 31%

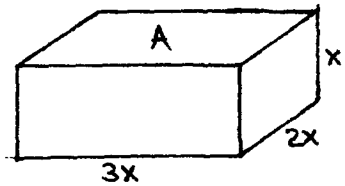
Area Factor = 1.00 - .31 = .69

PERTINENT AREAS

Tube	Inside Diameter Inches	Inside Diameter cm	Inside Area cm^2
1/2" Brass	0.622	1.58	1.96
3/4" Brass	0.824	2.09	3.43
1" Brass	1.049	2.66	5.55
Glass	1.875	4.77	17.90

FLOW AREA CORRECTION - interference of flow by various size crystals.

Sinse correction is small, assume crystal has a simple shape:



$$A = 6x^2$$

$$V = 6x^3 = \frac{W}{\rho} = \frac{W}{2.286}$$

Weight Crystal	Volume cm3	X cm	Area (3x)(2x)
20.0 mgm	.00875	.1135	.08 cm^2
30.0	.0131	.130	.10
40.0	.0175	.143	.12
10.0	.00437	.090	.05
50.0	.0218	.154	.14

For simplicity, an area crystal correction for the glass tube for 4 crystals = 0.33 cm^2 and correction for the brass tubes is assumed to be 0.07 cm^2.

CORRECTED TUBE AREAS

Glass tube	IA = 17.90 x .69 - 0.33 = 12.0 cm^2
1/2" Brass	IA = 1.96 x .69 - 0.07 = 1.28
3/4" Brass	IA = 3.43 x .69 - 0.07 = 2.29
1" Brass	IA = 5.55 x .69 - 0.07 = 3.76

VELOCITIES

(1) Sample calculation: At a rheostat setting of 65 the flow rate is 2000 cc per minute through the glass tube. Calculate velocity.

$$u = \frac{2000}{60} \frac{cm^3}{sec} \times \frac{1}{12.0\ cm^2} = 2.78 \frac{cm}{sec}$$

(2) Sample calculation: At a rheostat setting of 65 the flow rate is 1580 cc per minute through the brass tubes. Calculate velocity in 1/2" tube.

$$u = \frac{1580}{60} \frac{cm^3}{sec} \times \frac{1}{1.28\ cm^2} = 20.6 \frac{cm}{sec}$$

CALCULATION - conversion of Hixson Data

GROWTH RATE - For comparative purposes

convert:

$$w_{af} \frac{\#\,mol}{hr\,ft^2} \longrightarrow G \frac{mgm}{min \cdot mm^2} \longrightarrow R_D \frac{microns}{min}$$

calc:

$$w_{af} \frac{\#\,mol}{hr\,ft^2} \times 249.7 \frac{\#}{\#\,mol} \times 454000 \frac{mgm}{\#} \times \frac{1}{60} \frac{hr}{min} \times \frac{1}{305^2} \frac{ft^2}{mm^2}$$

$$w_{af} \times 20.4 = G$$

From the growth rate conversion plot (Figure IIA)

R_D = 1470 G , and

$$R_D = 1470\,(20.4\,w_{af})$$

$$R_D = 30{,}000\ w_{af}$$

Thus, to convert Hixson's growth values to the units used in this work, multiply by a factor of 30,000.

DEGREE OF SUPERSATURATION - For comparative purposes

convert:

$$(y_v - y_i) \frac{mol\ CuSO_4 \cdot 5H_2O}{total\ mols} \longrightarrow \Delta C \frac{grams\ CuSO_4 \cdot 5H_2O}{100\ gms\ free\ water}$$

calc:

(1) $\Delta y = y_v - y_i$

(2) $C_v = \frac{y_v}{1-y_v} \times \frac{250}{18} \times 100$; $C_i = \frac{y_i}{1-y_i} \times \frac{250}{18} \times 100$

(3) $\Delta C = 1390 \left[\frac{y_v}{1-y_v} - \frac{y_i}{1-y_i} \right] = \frac{1390\,\Delta y}{1 - y_v - y_i + y_i y_v}$

(4) Assume $y_i y_v$ in denominator to be negligible,

simplify: $$\Delta C = 1390 \left[\frac{\Delta y}{1 - 2 y_v} \right]$$

PERTINENT DATA

Exp't. No.	Solution Concentration C_B	Growth Temp. °C. T_2	Degree Supersat'n ΔC	Growth Rate R_D	Velocity u	Reynolds Number	
FIRST SERIES							
5	45.7	27.4	1.9	3.67	3.04	815	
6	45.45	27.35	1.7	2.56	"	820	
7	45.4	27.8	1.3	3.16	"	825	
8	44.7	27.8	0.5	1.41	"	840	
SECOND SERIES							
10	63.24	47.3	-0.51	-9.9	3.04		Dissolution
11	63.57	45.2	2.57	7.75	"	930	Reject run
12	63.57	44.1	3.82	16.7	"	905	
13	63.57	44.2	3.72	22.6	"	905	
14	63.90	42.0	6.60	46.0	"	975	
15	63.90	45.8	2.10	12.4	"	940	
THIRD SERIES							
16	62.25	42.4	4.50	22.8	2.8	825	
17	62.58	42.9	4.23	22.8	"	825	
18	62.91	44.0	3.31	17.8	"	875	
19	64.23	45.3	2.75	13.8	"	850	
20		46.5	1.53	5.4	"	875	Reject run
FOURTH SERIES							
22Y	60.60	42.2	3.10	23.7	11.5	1500	
22Z	60.60	42.2	3.10	20.6	7.0	1160	
23Z	60.60	40.3	5.00	32.1	4.3	690	
24Y	60.60	39.9	5.40	47.0	7.0	865	
24Z	60.60	39.9	5.40	38.8	4.3	680	
FIFTH SERIES							
25X	63.90	40.9	7.65	63.5	20.6	1910	
25Y	63.90	40.9	"	58.5	11.5	1410	
26X	63.90	40.4	8.20	61.7	20.6	1900	
26Y	63.90	40.4	"	55.7	11.5	1400	
26Z	63.90	40.4	"	42.6	7.0	1090	
27X	63.90	43.3	5.10	40.8	20.6	2000	
27Y	63.90	43.3	"	30.1	11.5	1480	
27Z	63.90	43.3	"	27.6	7.0	1140	
28X	64.56	46.5	1.91	21.1	20.6	2110	
28Y	64.56	46.5	"	22.5	11.5	1560	
28Z	64.56	46.5	"	18.0	7.0	1210	
29X	65.55	45.0	4.75	45.1	20.6	2070	
29Y	65.55	45.0	"	37.5	11.5	1530	
29Z	65.55	45.0	"	34.1	7.0	1180	

PERTINENT DATA

Exp't. No.	Solution Concentration C_B	Growth Temp. °C. T_2	Degree Supersat'n ΔC	Growth Rate R_D	Velocity u	Reynolds Number	
SIXTH SERIES							
30	63.4	46.4	0.9	4.77	2.8	870	
31	63.9	45.2	2.9	11.5	2.8	850	
32							Dissolution
33	64.2	45.8	2.4	8.66	3.0	920	
34	64.3	38.4	10.6	39.8	2.8	750	
36	64.6	42.8	6.4	31.0	2.8	800	
SEVENTH SERIES							
38	52.8	35.5	1.9	8.84	2.8	810	
39	53.1	36.4	1.3	4.64	2.8	820	
40	52.5	34.6	2.4	10.4	2.8	800	
41					No Growth - Sat'n Temp		
42	52.5	32.2	4.6	15.1	2.8	765	
43	52.8	33.5	3.8	17.0	2.8	775	
44	52.5	30.1	6.4	26.9	2.8	730	
EIGHTH SERIES							
45X	51.8	35.5	0.9	8.30	20.6	2010	
45Y	51.8	35.5	0.9	2.8		Rejected Run	
45Z	51.8	35.5	0.9	7.07	7.0	1150	
46X	51.8	35.5	0.9	5.06	20.6	2010	
46Y	51.8	35.5	0.9	6.87	11.5	1480	
46Z	51.8	35.5	0.9	6.35	7.0	1150	
47X	52.37	34.1	2.72	21.3	20.6	1930	
47Y	52.37	34.1	2.72	21.0	11.5	1420	
47Z	52.37	34.1	2.72	19.2	7.0	1100	
48X	52.95	32.2	5.05	37.6	20.6	1840	
48Y	52.95	32.2	5.05	35.4	11.5	1360	
48Z	52.95	32.2	5.05	31.3	7.0	1050	
49X	52.95	30.85	6.20	42.0	20.6	1800	
49Y	52.95	30.85	6.20	47.6	11.5	1330	
49Z	52.95	30.85	6.20	38.3	7.0	1030	

PERTINENT DATA

Exp't. No.	Solution Concentration C_B	Growth Temp. °C. T_2	Degree Supersat'n ΔC	Growth Rate R_D	Velocity u	Reynolds Number
NINTH SERIES						
50A	43.7	24.8	2.3	5.43	2.2	590
50X	43.7	25.0	2.1	8.24	20.6	1820
50Y	43.7	25.0	2.1	6.32	11.5	1340
50Z	43.7	25.0	2.1	6.47	7.0	1040
51A	43.7	24.8	2.2	5.16	2.2	590
51X	43.7	24.8	2.2	6.83	20.6	1850
51Y	43.7	24.8	2.2	7.47	11.5	1360
51Z	43.7	24.8	2.2	6.81	7.0	1050
52A	43.95	26.0	1.35	2.26	2.2	590
52X	43.95	26.0	1.35	3.87	20.6	1840
52Y	43.95	26.0	1.35	3.50	11.5	1360
52Z	43.95	26.0	1.35	3.16	7.0	1050
TENTH SERIES						
53A	80.1	57.8	1.5	8.92	2.2	712
54A	80.3	58.3	1.0	5.47	2.2	715
55	77.87	58.5	-1.7	-13.5	2.8	Dissolution
56	78.24	56.8	1.1	9.66	2.8	912
57	78.24	55.1	3.54	22.3	2.8	880
58		NO GROWTH - SATURATION				
59	78.4	53.6	5.8	39.8	2.8	854
60A	78.6	55.1	3.9	24.8	2.2	690
60X	78.6	55.1	3.9	60.7	20.6	2140
60Y	78.6	55.1	3.9	50.7	11.5	1590
60Z	78.6	55.1	3.9	44.0	7.0	1230
9						Rejected Run
21Z	60.60	45.6	0.62		Dissolution, Reject	
35	64.5	48.2	-.4	-6.66	2.8	Dissolution
37	65.2	49.4	-1.1	-21.6	2.8	Dissolution

PRIMARY DATA - SUMMARY

xp't. No.	Initial Weight Crystal mgm	Final Weight Crystal mgm	Cube Root Difference	Growth Time Minutes	Average Growth Temp.	Baume of Solution	Notes
	w_1	w_2	$\Delta(W^{1/3})$	θ	T_2	Be_2^{60}	
5 a	2.6	Lost	-				Mossy
b	9.7	16.4	0.408				Growth
c	14.9	22.6	0.367	118	27.4°	25.8°	on
d	19.1	28.4	0.376				crystals
e	23.5	33.2	0.349				
f	34.2	50.2	0.445				
Avg.			0.389 avg.				
6 a	6.7	8.4	0.147				
b	13.6	15.9	0.128				
c	19.8	23.1	0.142	60	27.35°	25.7°	
d	30.0	34.4	0.143				
e	14.7	17.1	0.127				
f	21.1	24.4	0.136				
Avg.			0.137 avg.				
7 a	8.4	10.9	0.186				
b	15.9	20.4	0.217				
c	23.1	28.6	0.209	73	27.8°	25.67°	
d	34.4	41.4	0.210				
e	17.1	21.3	0.196				
f	24.4	30.0	0.208				
Avg.			0.204 avg.				
8 a	10.8	13.8	0.189				
b	20.3	23.5	0.136	120	27.8°	25.4°	
c	28.0	31.8	0.130				
d	41.0	46.4	0.146				
Avg.			0.150 avg.				
9 a	7.7	12.9	0.374				Much mossy
b	19.1	28.9	0.394				growth on
c	27.2	39.2	0.390	54	45.1°	32.3°	crystals
d	36.7	49.0	0.336				Reject run
Avg.			0.374 avg.				
0 a	9.4	3.8	-0.551				
b	18.1	8.5	-0.586				
c	22.3	11.7	-0.544	65	47.3°	31.8°	Dissolution
d	25.1	12.2	-0.625				
Avg.			-0.577				

PRIMARY DATA - SUMMARY

Exp't. No.		Initial Weight Crystal mgm	Final Weight Crystal mgm	Cube Root Difference	Growth Time Minutes	Average Growth Temp.	Baume of Solution	Notes
		W_1	W_2	$\Delta(W^{1/3})$	θ	T_2	Be_2^{60}	
1	a	8.0	14.5	0.441				
	b	14.4	23.5	0.430				
	c	15.7	24.2	0.388	60	45.2°	31.9°	
	d	26.3	38.5	0.405				
Avg.				0.416 avg.				
2	a	7.1	21.7	0.866				Slight moss growth on crystals
	b	11.6	36.5	1.054	60	44.1°	31.9°	
	c	16.1	37.6	0.823				
	d	33.7	66.5	0.823				
Avg.				0.892 avg.				
3	a	14.5	27.7	0.587				
	b	23.5	41.4	0.595				
	c	24.2	43.3	0.620	30	44.2°	31.9°	
	d	38.5	64.0	0.620				
Avg.				0.606 avg.				
	a	6.1	25.2	1.104				Slight mossy Growth on crystals
	b	10.8	27.8	0.818				
	c	15.3	32.9	0.719	20	42.0°	32.0°	
	d	16.8	32.7	0.637				
Avg.				0.820 avg.				
	a	7.2	11.8	0.347				
	b	14.2	21.0	0.337				
	c	20.6	28.4	0.309	30	45.8°	32.0°	
Avg.				0.331 avg.				
	a	15.8	29.4	0.577				
	b	19.5	35.0	0.578				
	c	23.8	42.4	0.611	29	42.4°	31.5°	
Avg.				0.589 avg.				
	a	11.1	22.2	0.579				
	b	15.5	30.0	0.612				
	c	24.3	43.9	0.631	30	42.9°	31.6°	
Avg.				0.607 avg.				

PRIMARY DATA - SUMMARY

xp't. No.		Initial Weight Crystal mgm	Final Weight Crystal mgm	Cube Root Difference	Growth Time Minutes	Average Growth Temp.	Baume of Solution	Notes
		W_1	W_2	$\Delta(W^{1/3})$	θ	T_2	Be_2^{60}	
8	a	10.0	21.5	0.626				
	b	14.5	34.4	0.812	45	44.0°	31.7°	
	c	19.9	40.0	0.712				
Avg.				0.717 avg.				
9	a	9.3	19.1	0.572				
	b	18.3	33.1	0.574	45	45.3°	32.0°	
	c	26.2	42.2	0.514				
Avg.				0.553 avg.				
0	a	12.0	17.8	0.322				
	b	19.3	27.0	0.314	60	46.5°	32.1°	
	c	25.4	36.9	0.390				
Avg.				0.342 avg.				
1	X	23.7	Lost	x				Crystal fell thru basket
n. at'd.	Y	28.4	Lost	x	30	45.6°	31.0°	"
	Z	29.3	13.8	-0.683				Dissolution Reject Run
2	X	21.5	Lost	x				
	Y	29.9	52.1	0.632	30	42.2°	31.0°	
	Z	19.2	33.7	0.550				
3	X	33.7	Lost	x				
	Y	15.5	Lost	x	20	40.3°	31.0°	
	Z	14.9	27.9	0.570				
4	X	15.5	Lost					
	Y	18.3	41.8	0.836	20	39.9°	31.0°	
	Z	20.0	39.4	0.689				

PRIMARY DATA - SUMMARY

Exp't. No.		Initial Weight Crystal mgm	Final Weight Crystal mgm	Cube Root Difference	Growth Time Minutes	Average Growth Temp.	Baume of Solution	Notes
		ω_1	ω_2	$\Delta(\omega^{1/3})$	θ	T_2	Be_2^{60}	
25	X	20.6	58.0	1.130				
	Y	16.4	45.8	1.038	20	40.9°	32.0°	
	Z	20.6	Lost	x				
26	X	13.9	43.0	1.099				
	Y	19.1	49.1	0.988	20	40.4°	32.0°	
	Z	28.9	56.0	0.758				
27	X	13.5	30.0	0.725				
	Y	15.1	27.2	0.535	20	43.3°	32.0°	
	Z	14.4	25.0	0.490				
28	X	15.1	23.1	0.376				
	Y	16.2	25.2	0.401	20	46.5°	32.2°	
	Z	21.2	29.5	0.320				
29	X	16.0	36.7	0.803				
	Y	22.0	41.7	0.667	20	45.0°	32.5°	
	Z	21.7	39.2	0.609				
0	a	14.8	16.7	0.101				
	b	21.7	23.4	0.070	20	46.4°	31.85°	
	c	32.2	34.8	0.085				
Avg.				0.085 avg.				
1	a	16.7	21.2	0.212				
	b	23.4	28.2	0.184	20	45.2°	32.0°	
	c	34.8	42.2	0.220				
Avg.				0.205 avg.				

PRIMARY DATA - SUMMARY

xp't. No.	Initial Weight Crystal mgm	Final Weight Crystal mgm	Cube Root Difference	Growth Time Minutes	Average Growth Temp.	Baume of Solution	Notes
	W_1	W_2	$\Delta(W^{1/3})$	θ	T_2	Be_2^{60}	
2 a	21.2	19.1	-0.094				Dissolution
td. b	28.2	27.2	-0.035	20	47.4°	32.0°	Poor Growth
n. c	42.2	41.8	-0.009				Checks
Avg.			-0.046 avg.				
3 a	19.1	23.3	0.182				Velocity slightly
b	27.2	31.3	0.142	20	45.8°	32.1°	higher than
c	41.8	47.1	0.139				rest of series.
Avg.			0.154 avg.				By error.
4 a	23.3	44	0.676				Slight moss on
b	31.3	54	0.629	18	38.4°	32.1°	crystals- time
c	47.1	75	0.608				cut short due to "breaking"
Avg.			0.638 avg.				of soln - High supersaturation
5 a	18.6	15.7	-0.144				Dissolution
td. b	19.5	17.5	-0.093	20	48.2°	32.2°	
n. c	22.8	20.0	-0.121				
Avg.			-0.119 avg.				
a	15.7	28.2	0.540				
b	17.5	32.5	0.592	20	42.8°	32.2°	
c	20.0	34.2	0.532				
Avg.			0.554 avg.				
a	20.8	16.6	-0.199	10	49.4°	32.4°	Dissolution
td. b	40.3	34.2	-0.185				
n.			-0.192 avg.				
a	10.0	13.6	0.233				
b	16.3	21.1	0.229	30	35.5°	28.45°	
c	24.4	31.1	0.245				
Avg.			0.236 avg.				
a	13.6	15.4	0.101				
b	21.1	24.3	0.133	30	36.4°	28.55°	
c	31.1	35.4	0.138				
Avg.			0.124 avg.				

PRIMARY DATA - SUMMARY

Exp't. No.		Initial Weight Crystal mgm	Final Weight Crystal mgm	Cube Root Difference	Growth Time Minutes	Average Growth Temp.	Baume of Solution	Notes
		W_1	W_2	$\Delta(W^{1/3})$	Θ	T_2	$Bé^{60}$	
40	a	15.4	19.4	0.199				
	b	24.3	28.9	0.170	20	34.6°	28.35°	
	c	35.4	41.5	0.182				
Avg.				0.184 avg.				
41	a	19.4	19.4	No Growth				Result checks solubility data
td.	b	28.9	29.0		20	37.2°	28.45°	
n)	c	41.5	41.3					
Avg.								
42	a	19.4	26.0	0.276				
	b	29.0	36.8	0.255	20	32.2°	28.35°	
	c	41.3	51.9	0.272				
Avg.				0.268 avg.				
43	a	7.7	Lost	x				
	b	12.7	17.8	0.277	20	33.5°	28.45°	
	c	21.6	30.2	0.328				
Avg.				0.303 avg.				
44	a	17.8	30.3	0.506				
	b	30.2	46.2	0.475	20	30.1°	28.35°	
	c	36.8	54.0	0.454				
Avg.				0.478 avg.				
45	X	17.6	22.5	0.222				
	Y	16.9	18.4	0.074*	30	35.5°	28.1°	*Reject 45Y low result
	Z	14.3	17.9	0.189				
46	X	22.5	29.6	0.270*				*Low
	Y	18.4	27.2	0.367	60	35.5°	28.1°	
	Z	17.9	25.8	0.339				

PRIMARY DATA - SUMMARY

Exp't. No.		Initial Weight Crystal mgm	Final Weight Crystal mgm	Cube Root Difference	Growth Time Minutes	Average Growth Temp.	Baume of Solution	Notes
		W_1	W_2	$\Delta(W^{1/3})$	Θ	T_2	Be_2^{60}	
47	X	23.0	39.8	0.570				
	Y	22.2	38.3	0.560	30	34.1°	28.3°	
	Z	27.6	43.4	0.512				
48	X	23.8	44.6	0.670				
	Y	32.5	55.8	0.630	20	32.2°	28.5°	
	Z	20.4	35.6	0.558				
49	X	19.1	41.4	0.786				
	Y	18.2	43.6	0.890*	21	30.85°	28.5°	*High
	Z	22.4	44.2	0.717				
50	a	14.2	19.7	0.279				
	b	20.4	28.1	0.308		24.8°		$u = 2.2 \frac{cm}{sec.}$
	c	21.8	29.1	0.282				
	Avg.			0.290 avg.	60		25.0°	
	X	15.1	24.7	0.440				$u = 20.6$
	Y	13.5	20.1	0.338		25.0°		$u = 11.5$
	Z	17.9	26.0	0.346				$u = 7.0$
51 A	a	19.7	26.5	0.280				
	b	28.1	35.9	0.259				
	c	29.1	38.1	0.289				
	Avg.			0.276 avg.	60	24.8°	25.0°	
	X	24.7	35.2	0.365				
	Y	20.1	30.3	0.399				
	Z	26.0	36.8	0.364				

PRIMARY DATA - SUMMARY

Exp't. No.		Initial Weight Crystal mgm	Final Weight Crystal mgm	Cube Root Difference	Growth Time Minutes	Average Growth Temp.	Baume of Solution	Notes
		W_1	W_2	$\Delta(W^{1/3})$	Θ	T_2	Be_2^{60}	
52	a	26.5	29.6	0.112				
A	b	35.9	40.3	0.129				
	c	38.1	42.4	0.122				
Avg.				0.121 avg.	60	26.0°	25.1°	
	X	35.2	42.3	0.207				
	Y	30.3	36.1	0.187				
	Z	36.8	42.7	0.169				
53	a	16.3	19.8	0.170				
A	b	46.0	51.9	0.147	20	57.8°	36.7°	
Avg.				0.159 avg.				
54	a	19.8	22.0	0.097				
A	b	36.2	39.5	0.098	20	58.3°	36.75°	
Avg.				0.0975 avg.				
55	a	22.0	Lost	x				
A	b	39.5	31.7	-0.241	20	58.5°	36.1°	Dissolution
Avg. satd. ln)				-0.241 avg.				
56	a	19.5	23.5	0.172				
	b	24.0	28.5	0.171	20	56.8°	36.2°	
Avg.				0.1715 avg.				
57	a	23.5	34.6	0.395				
	b	28.5	41.2	0.399	20	55.1°	36.2°	
Avg.				0.397 avg.				
58	a	34.6	34.4	0				No growth
	b	41.2	41.6	0	15	57.4°	36.15°	solubility
Avg.								Baume check.
59	a	34.4	62	0.706				
	b	41.6	73	0.714	20	53.6°	36.25°	
Avg.				0.710 avg.				

PRIMARY DATA - SUMMARY

p't. o.	Initial Weight Crystal mgm	Final Weight Crystal mgm	Cube Root Difference	Growth Time Minutes	Average Growth Temp.	Baume of Solution	Notes
	W_1	W_2	$\Delta(W^{1/3})$	θ	T_2	Be_2^{60}	
a	17.2	27.2	0.426				
b	30.3	45.7	0.457				
avg.			0.442 avg.	20	55.1°	36.3°	
X	19.8	54.3	1.082				
Y	17.4	42.7	0.904				
Z	14.6	33.6	0.783				

CALCULATED DATA

	Run	Solution Saturation Temp. °C.	Diameter Tube cm	Solution Velocity cm/sec.	Solution Density gm/cc	Solution Viscosity cp.	$\frac{R_D}{\Delta C}$	$\{R_D\}_{u=1}$	$\left[\frac{R_D}{\Delta C}\right]_{u=1}$
		T_s	D	u	ρ	μ			
	5	29.6	4.77	3.04	1.23	2.19	1.93	2.80	1.47
1	6	29.2	"	"	"	2.18	1.50	1.96	1.15
	7	29.2	"	"	"	2.16	2.44	2.41	1.85
	8	28.4	"	"	"	2.12	2.82	1.08	2.16
	12	47.2	4.77	3.04	1.29	2.06	4.38	12.0	3.14
2	13	47.2	"	"	"	2.06	6.08	16.3	4.38
	14	47.4	"	"	"	2.13	6.98	33.1	5.01
	15	47.4	"	"	"	1.99	5.90	8.9	4.23
	16	46.2	4.77	2.80	1.29	2.08	5.07	16.8	3.74
3	17	46.4	"	"	1.29	2.08	5.39	16.8	3.97
	18	44.7	"	"	1.28	1.97	5.37	13.1	3.96
	19	47.4	"	"	1.29	2.03	5.02	10.2	3.71
	22Y	44.8	2.09	11.5	1.28	2.06	7.65	11.6	3.74
	22Z	44.8	2.66	7.0	"	2.06	6.65	11.6	3.74
4	23Z	44.8	2.66	4.3	"	2.13	6.41	20.8	4.15
	24Y	44.8	2.09	7.0	"	2.16	8.70	26.6	4.92
	24Z	44.8	2.66	4.3	"	2.16	7.20	25.2	4.67
	25X	47.4	1.58	20.6	1.29	2.20	8.3	27.4	3.58
	25Y	"	2.09	11.5	"	2.20	7.65	28.6	3.74
	26X	47.4	1.58	20.6	"	2.21	7.52	26.6	3.24
	26Y	"	2.09	11.5	"	2.21	6.8	27.2	3.32
	26Z	"	2.66	7.0	"	2.21	5.2	24.0	2.93
	27X	47.4	1.58	20.6	"	2.10	8.0	17.6	3.45
5	27Y	"	2.09	11.5	"	2.10	5.9	14.7	2.88
	27Z	"	2.66	7.0	"	2.10	5.42	15.5	3.04
	28X	47.9	1.58	20.6	"	1.99	11.1	9.1	4.77
	28Y	"	2.09	11.5	"	1.99	11.8	11.0	5.75
	28Z	"	2.66	7.0	"	1.99	9.42	10.1	5.28
	29X	48.6	1.58	20.6	"	2.03	9.5	19.4	4.08
	29Y	"	2.09	11.5	"	2.03	7.9	18.3	3.85
	29Z	"	2.66	7.0	"	2.03	7.18	19.2	4.04
	30	47.0	4.77	2.8	1.29	1.97	5.3	3.50	3.90
	31	47.4	"	2.8	"	2.03	4.0	8.45	2.91
6	33	47.6	"	3.0	"	2.00	3.61	6.27	2.61
	34	47.6	"	2.8	"	2.30	3.76	29.2	2.75
	36	47.9	"	2.8	"	2.14	4.85	22.8	3.56
	38	37.4	4.77	2.8	1.26	2.08	4.65	6.69	3.52
	39	37.8	"	"	"	2.05	3.57	3.51	2.70
7	40	37.2	"	"	"	2.10	4.34	7.90	3.29
	42	37.2	"	"	"	2.20	3.28	11.4	2.48
	43	37.4	"	"	"	2.17	4.47	12.9	3.40
	44	37.2	"	"	"	2.30	4.20	20.4	3.19

CALCULATED DATA

	Run	Solution Saturation Temp. °C.	Diameter Tube cm	Solution Velocity cm/sec.	Solution Density gm/cc	Solution Viscosity cp.	$\frac{R_D}{\Delta C}$	$\{R_D\}_{u=1}$	$\frac{\{R_D\}_{u=1}}{\Delta C}$
		T_s	D	u	ρ	μ			
	45X	36.4	1.58	20.6	1.26	2.04	9.22	3.70	4.11
	45Y	"	rejected run						
	45Z	"	2.66	7.0	1.26	2.04	7.86	4.18	4.65
	46X	36.4	1.58	20.6	"	2.04	5.6		
	46Y	"	2.09	11.5	"	2.04	7.6	3.58	3.98
	46Z	"	2.66	7.0	"	2.04	7.1	3.76	4.17
	47X	37.0	1.58	20.6	"	2.13	7.83	9.5	3.50
8	47Y	"	2.09	11.5	"	2.13	7.70	10.9	4.01
	47Z	"	2.66	7.0	"	2.13	7.05	11.4	4.19
	48X	37.6	1.58	20.6	"	2.23	7.45	16.8	3.33
	48Y	"	2.09	11.5	"	2.23	7.00	18.4	3.64
	48Z	"	2.66	7.0	"	2.23	6.20	18.5	3.66
	49X	37.6	1.58	20.6	"	2.28	6.78	18.7	3.02
	49Y	"	2.09	11.5	"	2.28	7.68	24.8	4.00
	49Z	"	2.66	7.0	"	2.28	6.18	22.7	3.66
	50A	27.3	4.77	2.2	1.23	2.20	2.36	4.45	1.93
	X	"	1.58	20.6	"	"	3.92	3.96	1.88
	Y	"	2.09	11.5	"	"	3.01	3.51	1.67
	Z	"	2.66	7.0	"	"	3.08	4.01	1.91
	51A	27.3	4.77	2.2	"	2.17	2.34	4.23	1.92
	X	"	1.58	20.6	"	"	3.11	3.28	1.48
9	Y	"	2.09	11.5	"	"	3.40	4.15	1.89
	Z	"	2.66	7.0	"	"	3.10	4.23	1.92
	52A	27.6	4.77	2.2	"	2.18	1.67	1.85	1.37
	X	"	1.58	20.6	"	"	2.87	1.86	1.38
	Y	"	2.09	11.5	"	"	2.59	1.94	1.44
	Z	"	2.66	7.0	"	"	2.34	1.96	1.45
	53A	58.8	4.77	2.2	1.33	1.96	5.95	6.50	4.33
	54A	59.0	4.77	2.2	"	1.95	5.47	3.98	3.98
	56	57.6	4.77	2.8	"	1.95	8.78	6.37	5.79
	57	57.6	4.77	2.8	"	2.02	6.30	14.7	4.15
10	59	57.7	4.77	2.8	"	2.08	6.87	26.2	4.52
	60A	57.8	4.77	2.2	"	2.02	6.36	18.05	4.63
	60X	"	1.58	20.6	"	"	15.5	17.75	4.55
	60Y	"	2.09	11.5	"	"	13.0	18.8	4.82
	60Z	"	2.66	7.0	"	"	11.3	20.0	5.13

SUMMARY OF HIXSON DATA - (UNITS CONV RTED AND CALCULATED)

	Saturation Temp. °C.	Growth Rate $R_D = \mu/min$	Supersat'n $\Delta C = \frac{gm\ BV}{100 gm\ FW}$	Velocity $u =$ cm/sec	$\left(\frac{R_D}{\Delta C}\right)$	$\left[\frac{R_D}{u^m}\right]$
1	19.5°	4.05	3.54	2.39	1.15	
2	"	3.84	2.86	3.17	1.34	
3	"	4.80	2.40	6.0	2.00	
4	"	.74	0.70	33.6	1.06	
5	"	.77	0.70	33.6	1.10	
6	41.5°	7.62	2.32	31.7	3.28	2.95
7	"	6.57	1.78	16.8	3.69	3.00
8	"	2.94	1.61	1.7	1.83	2.40
9	"	1.82	.96	2.8	1.89	1.35
10	"	.94	.65	4.24	1.45	.61
11	"	2.22	1.30	2.56	1.71	1.62
12	"	1.50	.66	7.0	2.28	.86
13	"	3.30	1.29	11.0	2.56	1.75
14	"	2.72	.625	39.4	4.35	1.00
15	"	4.89	1.49	17.8	3.28	2.22
16	"	2.93	.87	28.6	3.37	1.17
17	53.4°	7.05	1.93	4.24	3.65	4.4
18	"	4.86	1.41	7.62	3.44	2.45
19	"	9.81	3.87	2.45	2.54	7.2
20	"	3.30	.78	11.0	4.23	1.48
21	"	8.91	1.29	31.0	6.90	2.8
22	"	14.79	3.24	9.75	4.57	6.9
23	"	12.0	1.46	18.0	8.21	3.4
24	"	5.37	.69	102.0	7.77	1.10
25	71.1°	18.66	1.13	112.0	16.5	1.01
26	"	49.26	2.63	56.0	18.7	4.07
27	"	27.24	1.58	95.0	17.2	1.61
28	"	24.09	1.90	61.0	12.7	1.88
29	"	12.81	1.09	110.0	12.3	.69
30	"	17.76	1.59	44.2	11.2	1.71
31	"	14.61	2.35	17.6	6.22	2.44
32	"	7.65	.90	36.6	8.50	.82
33	"	12.54	1.63	20.8	7.70	1.91
34	"	4.20	.82	11.7	5.12	.91
35	"	9.00	2.84	6.8	3.17	2.73
36	"	8.10	2.57	7.5	3.15	2.32
37	"	6.09	1.11	7.05	5.49	1.85
38	"	6.60	1.85	9.02	3.57	1.69

SUMMARY OF McCABE'S DATA (ΔC = 0.9)

$R_D = 1.22 R_L$

Reciprocating Cage Experiments

Runs	Velocity cm/sec.	Growth Rate R_L = μ/min	Growth Rate R_D = μ/min	$R_D/\Delta C$
180-183	.9	1.21	1.48	1.64
177-9	1.8	1.36	1.66	1.84
184-7	2.6	1.42	1.73	1.92
158-61	3.3	1.62	1.98	2.20
171-3	6.9	1.47	1.79	1.99
174-6	13.9	1.55	1.89	2.10

Stationary Cage Experiments

Runs	Velocity cm/sec.	Growth Rate R_L = μ/min.	Growth Rate R_D	$R_D/\Delta C$
188-91	.2	1.16	1.41	1.57
208-11	.6	1.41	1.72	1.91
192-5	1.0	1.53	1.87	2.08
211-15	1.4	1.61	1.96	2.18
196-9	1.9	1.71	2.08	2.31
216-19	2.3	1.80	2.20	2.44
200-3	2.7	1.92	2.34	2.60
220-222	2.7	1.85	2.26	2.51
204-7	3.6	1.92	2.34	2.60

FIGURE A

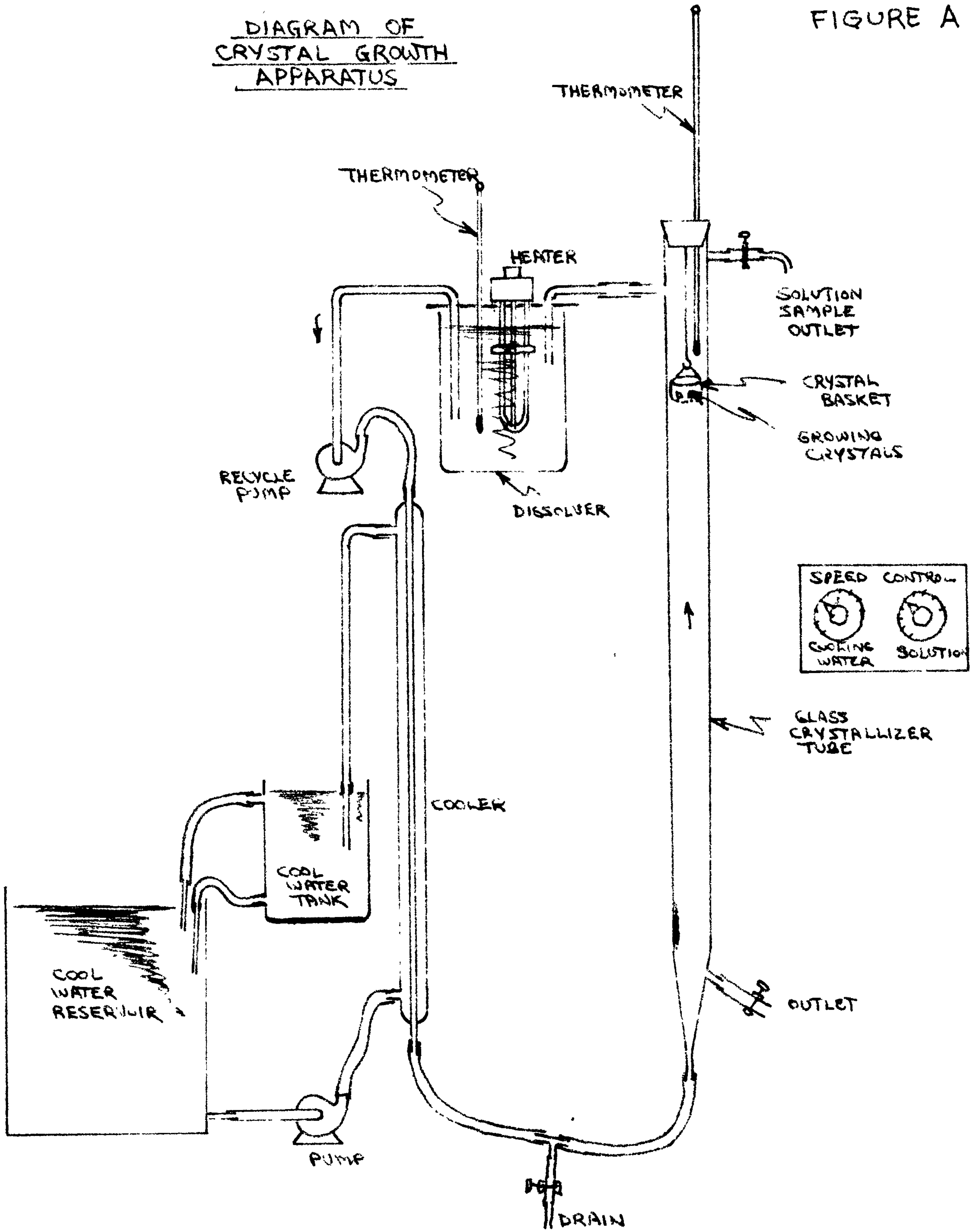


DIAGRAM OF
CRYSTAL GROWTH
APPARATUS
THERMOMETER
THERMOMETER
HEATER
SOLUTION
SAMPLE
OUTLET
CRYSTAL
BASKET
GROWING
CRYSTALS
RECYCLE
PUMP
DISSOLVER
SPEED CONTROL
COOLING
WATER
SOLUTION
GLASS
CRYSTALLIZER
TUBE
COOLER
COOL
WATER
TANK
COOL
WATER
RESERVOIR
OUTLET
PUMP
DRAIN

FIGURE B.

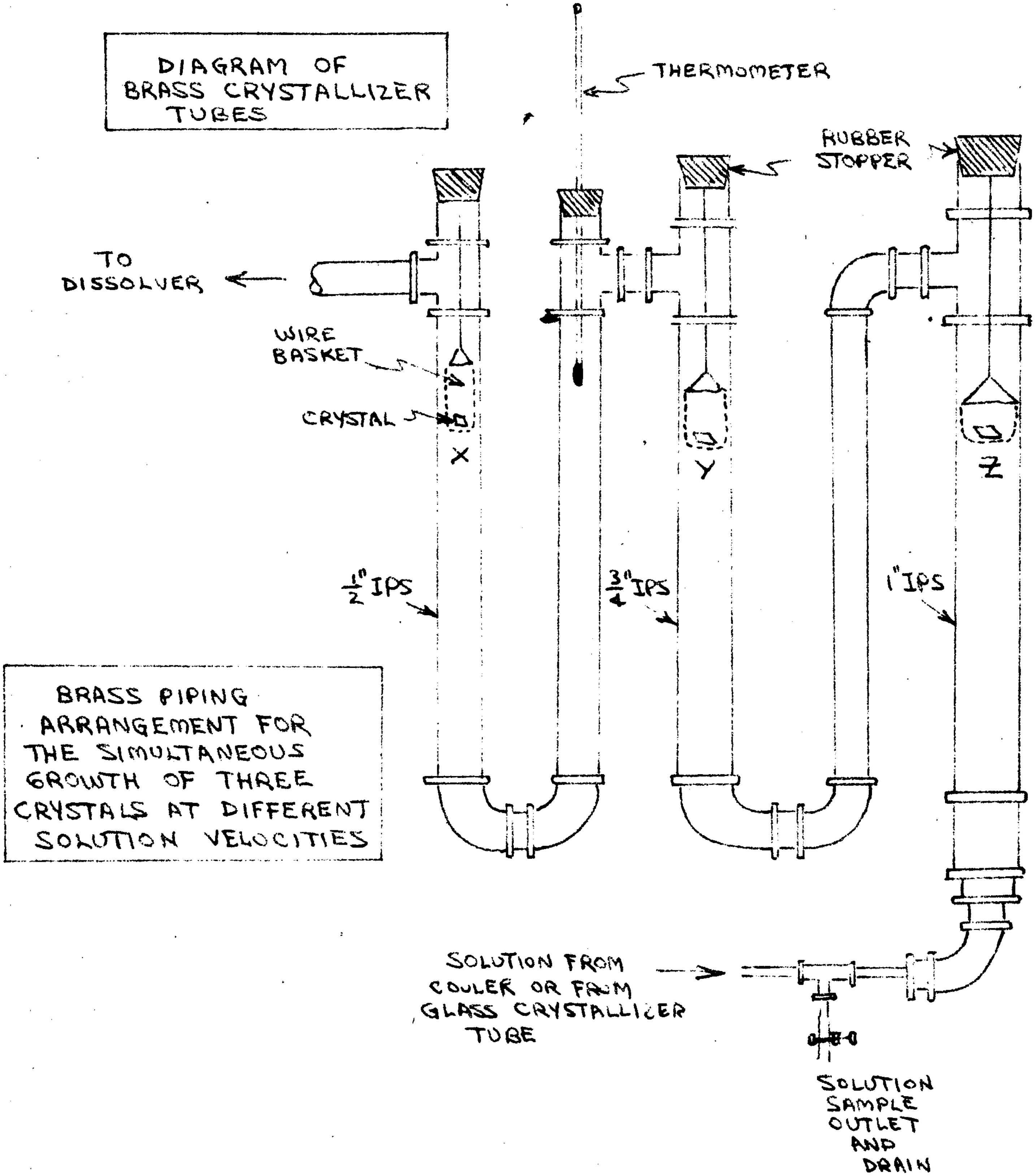
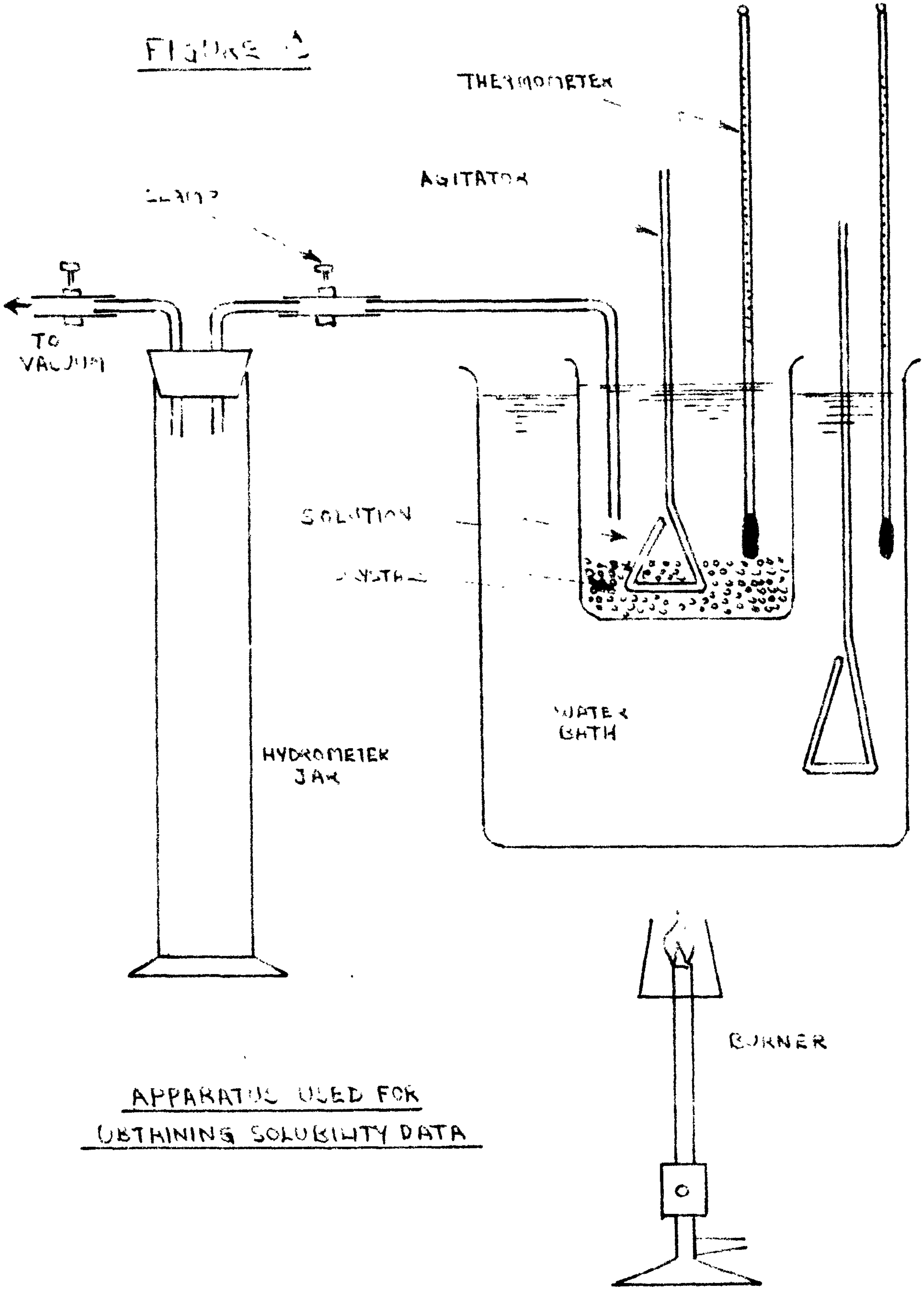


DIAGRAM OF BRASS CRYSTALLIZER TUBES
THERMOMETER
RUBBER STOPPER
TO DISSOLVER
WIRE BASKET
CRYSTAL
X
Y
Z
1/2" IPS
3/4" IPS
1" IPS
BRASS PIPING ARRANGEMENT FOR THE SIMULTANEOUS GROWTH OF THREE CRYSTALS AT DIFFERENT SOLUTION VELOCITIES
SOLUTION FROM COOLER OR FROM GLASS CRYSTALLIZER TUBE
SOLUTION SAMPLE OUTLET AND DRAIN

FIGURE 2



APPARATUS USED FOR OBTAINING SOLUBILITY DATA

FIGURE I

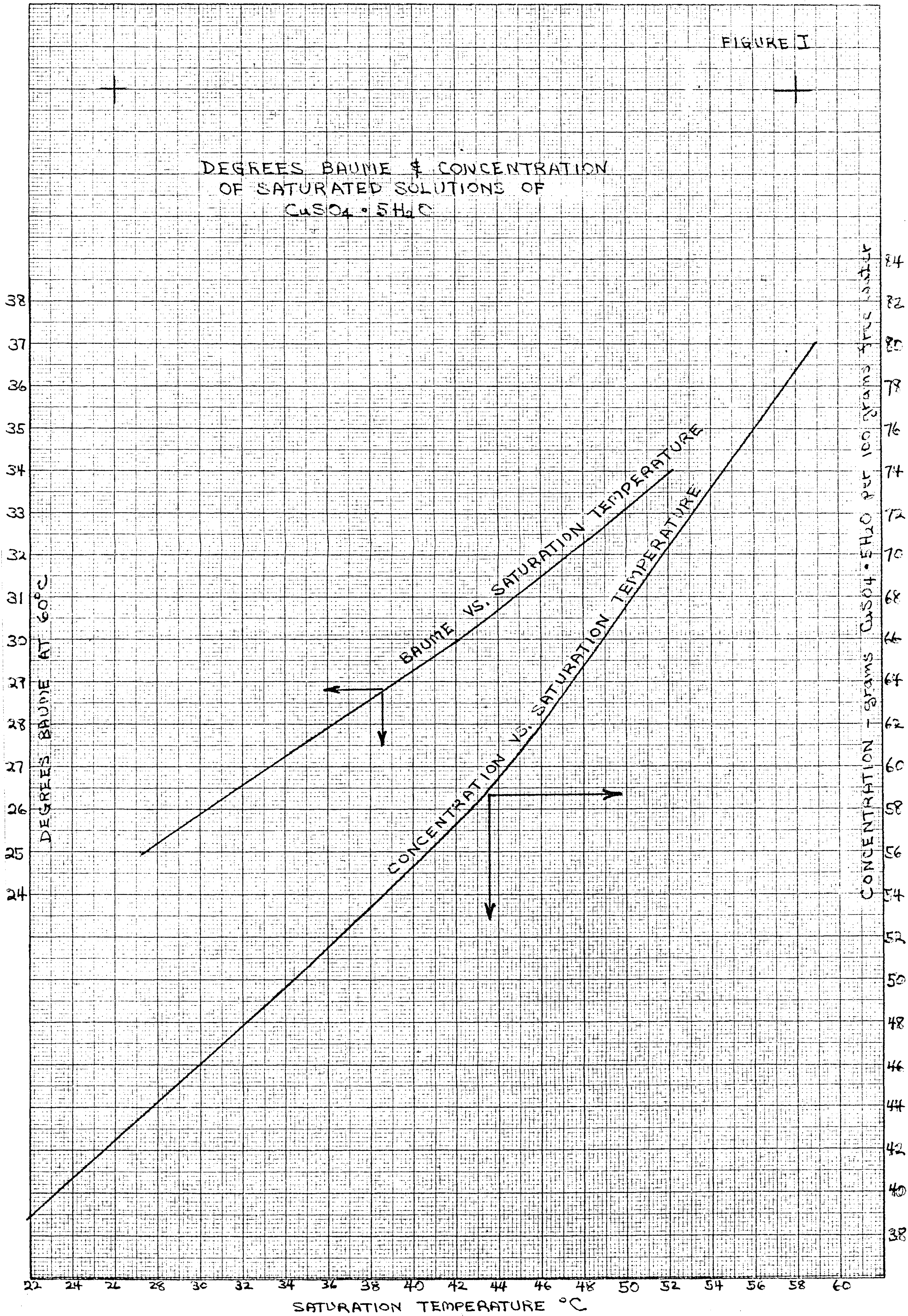

DEGREES BAUME & CONCENTRATION OF SATURATED SOLUTIONS OF $CuSO_4 \cdot 5H_2O$
BAUME VS. SATURATION TEMPERATURE
CONCENTRATION VS. SATURATION TEMPERATURE
DEGREES BAUME AT 60°C
CONCENTRATION - grams $CuSO_4 \cdot 5H_2O$ per 100 grams free water
SATURATION TEMPERATURE °C
38
37
36
35
34
33
32
31
30
29
28
27
26
25
24
84
82
80
78
76
74
72
70
68
66
64
62
60
58
56
54
52
50
48
46
44
42
40
38
22
24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60

FIGURE II

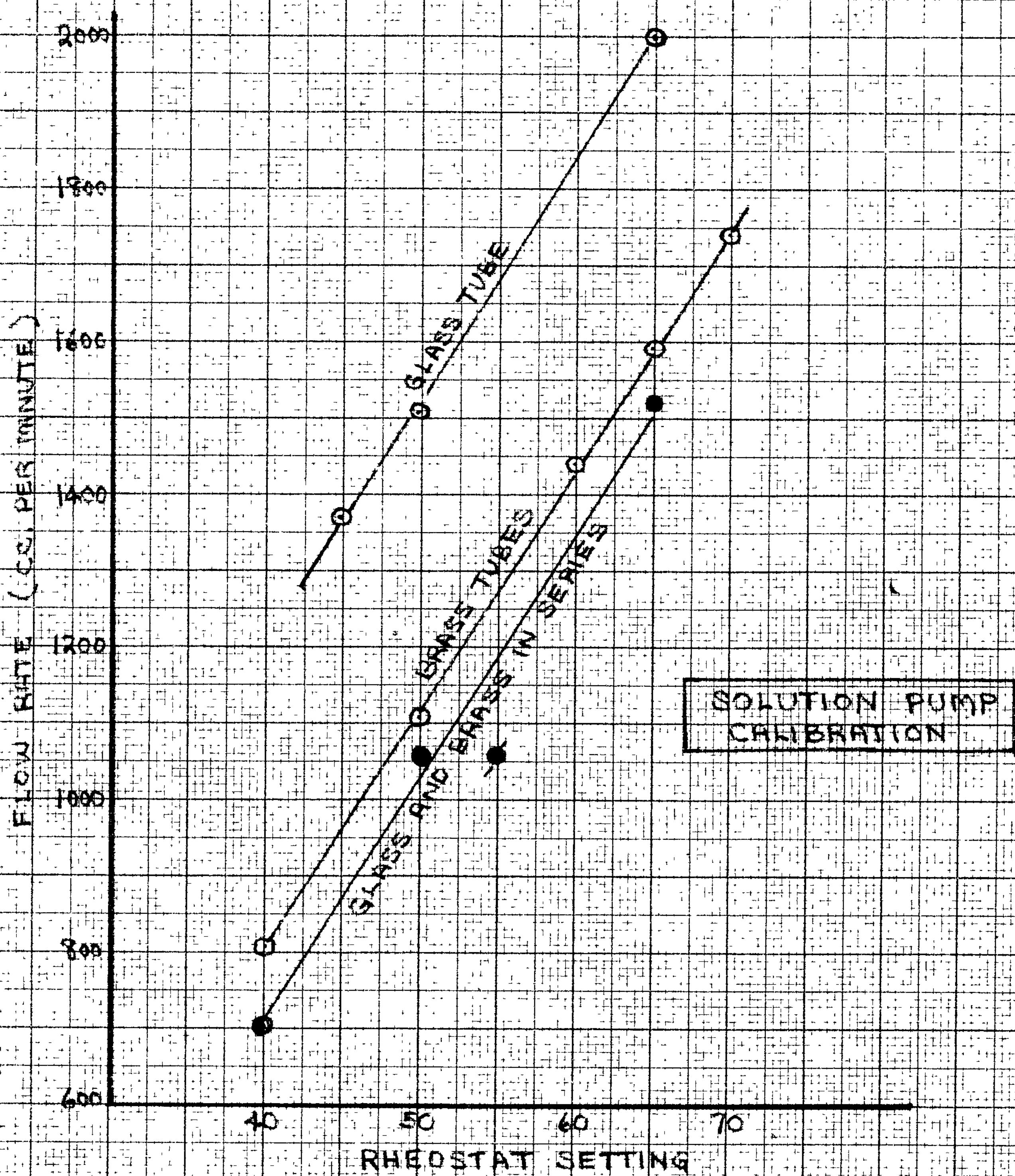
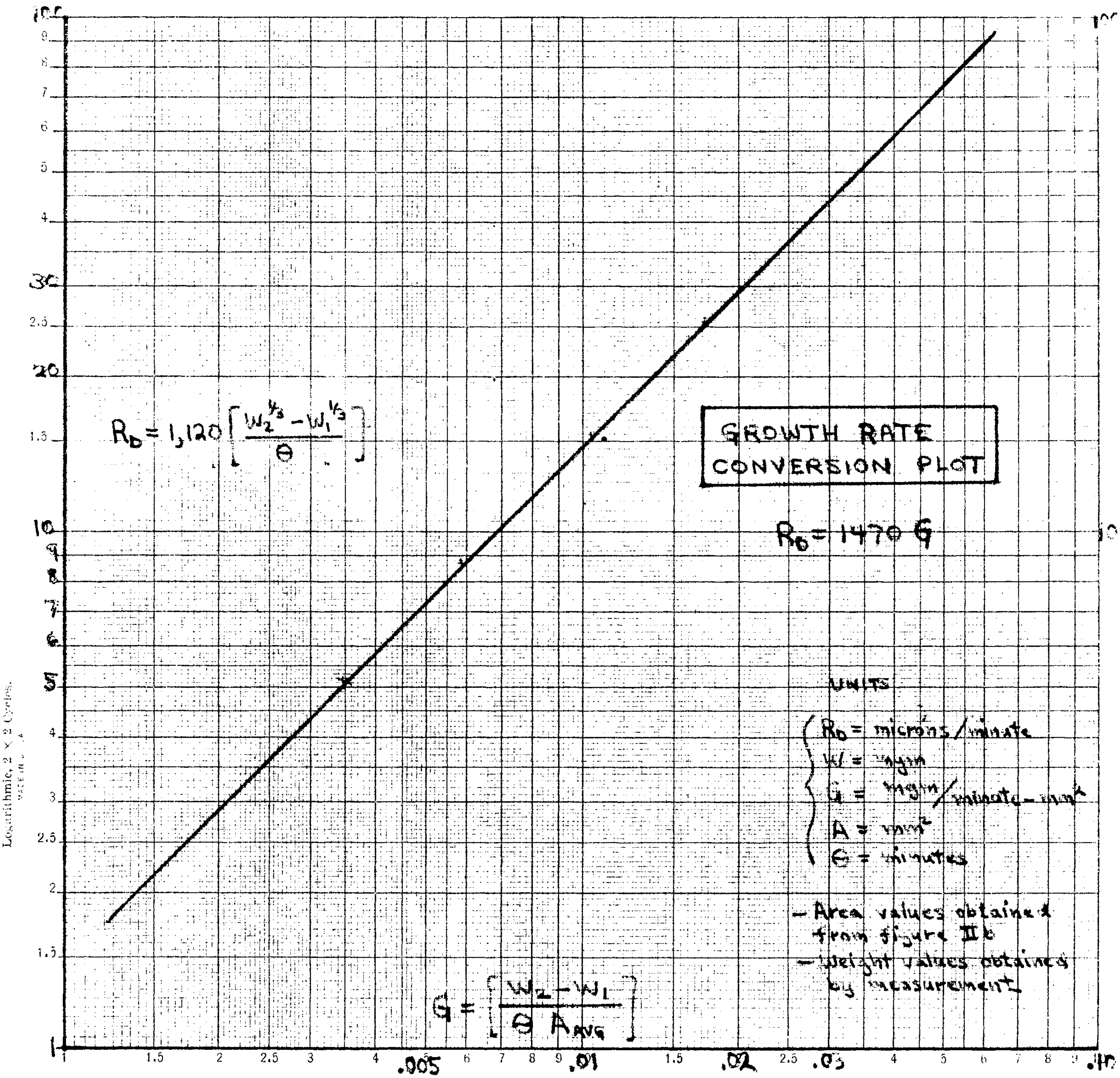

SOLUTION PUMP CALIBRATION
FLOW RATE (CC. PER MINUTE)
RHEOSTAT SETTING
GLASS TUBE
BRASS TUBES
GLASS AND BRASS IN SERIES
2000
1800
1600
1400
1200
1000
800
600
40
50
60
70

FIGURE IIA



GROWTH RATE CONVERSION PLOT
$R_b = 1,120 \left[\frac{W_2^{1/3} - W_1^{1/3}}{\Theta} \right]$
$R_b = 1470\, G$
UNITS
R_b = microns/minute
W = mgm
G = mgm/minute-mm²
A = mm²
Θ = minutes
– Area values obtained from figure IIb
– Weight values obtained by measurement
$G = \left[\frac{W_2 - W_1}{\Theta\, A_{AVG}} \right]$
.005
.01
.02
.03
.10

FIGURE 2B

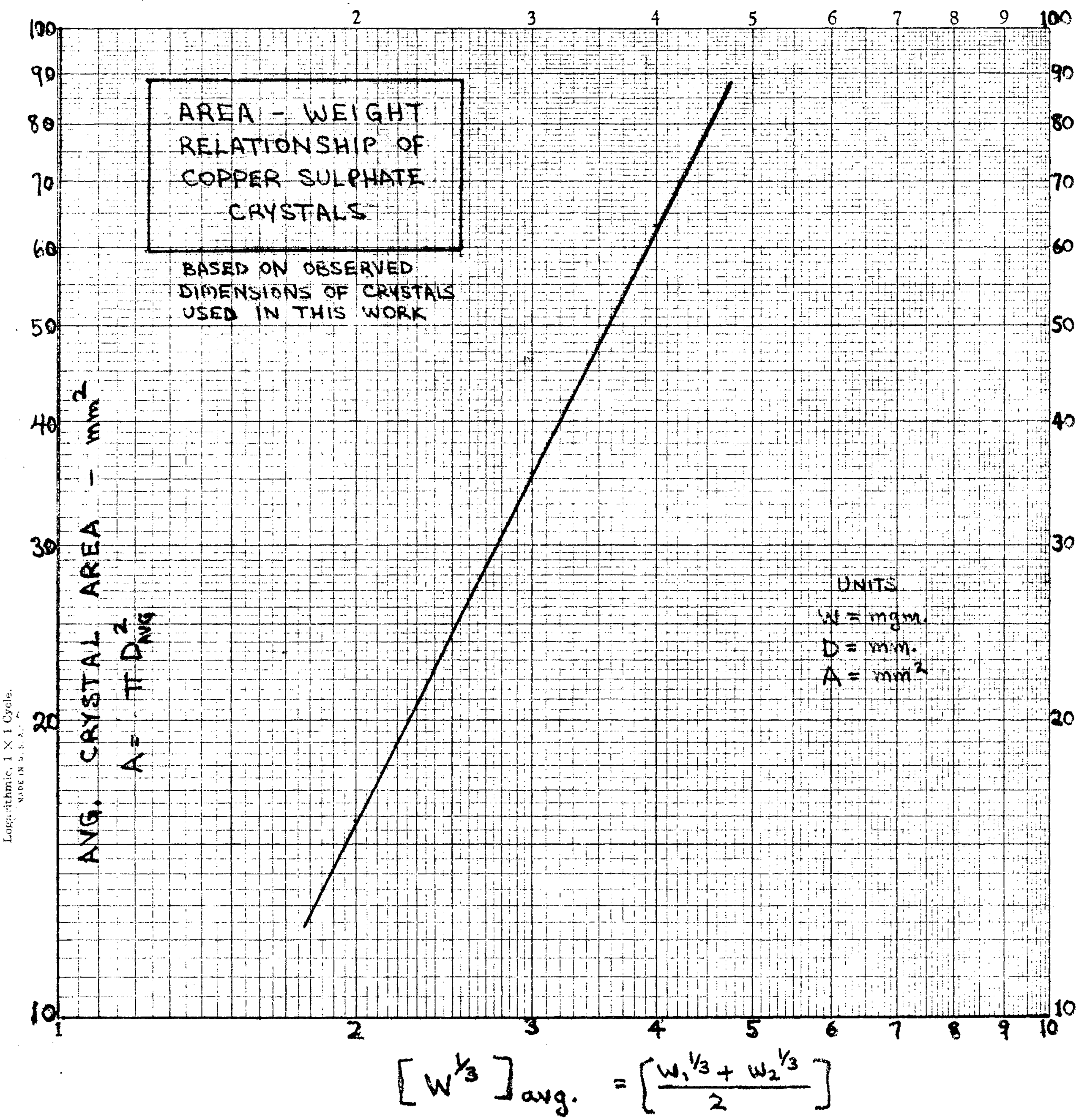
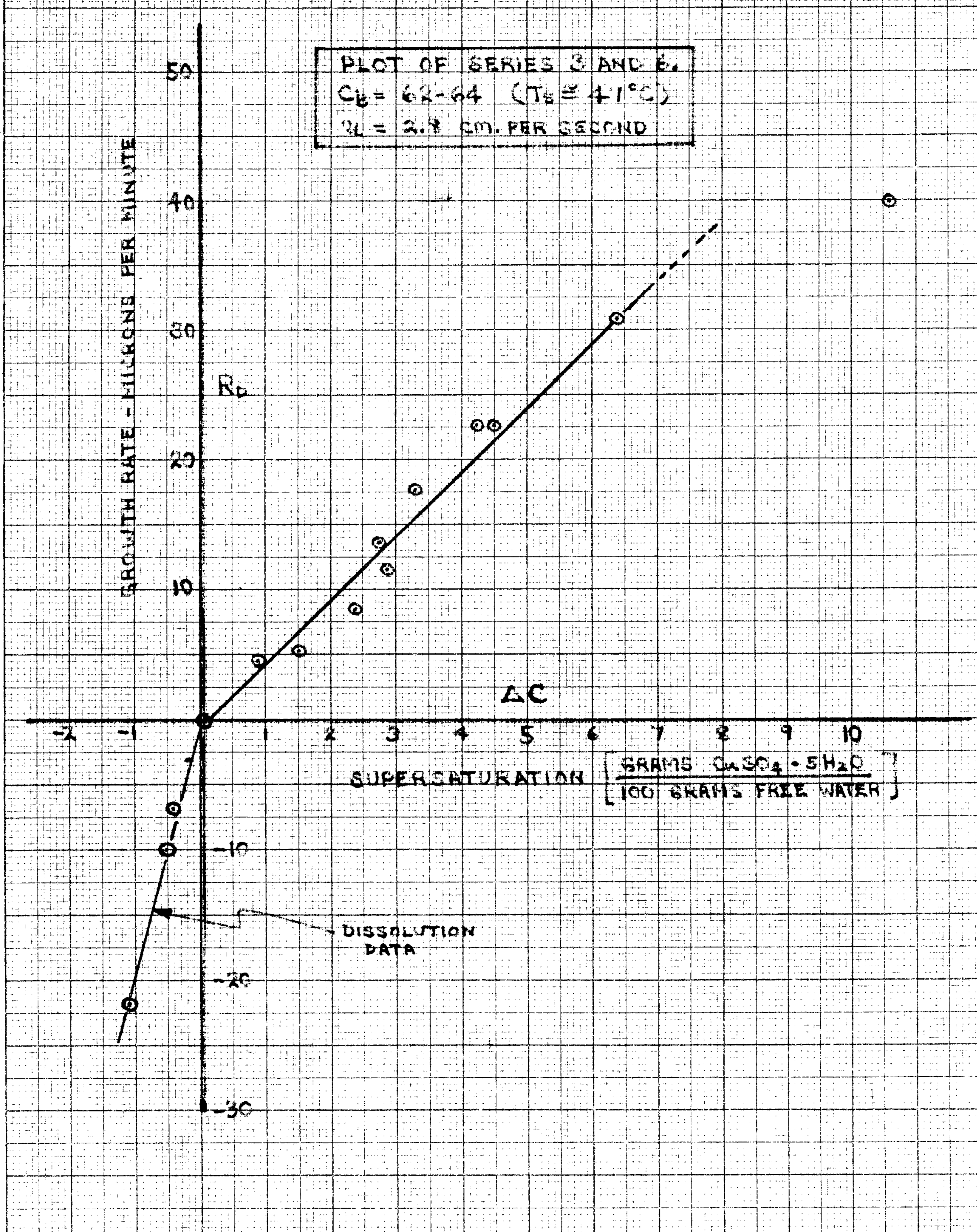

AREA - WEIGHT RELATIONSHIP OF COPPER SULPHATE CRYSTALS
BASED ON OBSERVED DIMENSIONS OF CRYSTALS USED IN THIS WORK
AVG. CRYSTAL AREA - mm²
A = π D²AVG
UNITS
W = mgm.
D = mm.
A = mm²
[W^1/3]avg. = [(W1^1/3 + W2^1/3)/2]
Logarithmic, 1 X 1 Cycle.
MADE IN U. S. A.

FIGURE III



PLOT OF SERIES 3 AND 6.
C_B = 62-64 (T_S ≅ 41°C)
v_L = 2.8 cm. PER SECOND
GROWTH RATE - MICRONS PER MINUTE
R_D
50
40
30
20
10
-10
-20
-30
ΔC
-2
-1
1
2
3
4
5
6
7
8
9
10
SUPERSATURATION [GRAMS $CuSO_4 \cdot 5H_2O$ / 100 GRAMS FREE WATER]
DISSOLUTION DATA

FIGURE IV

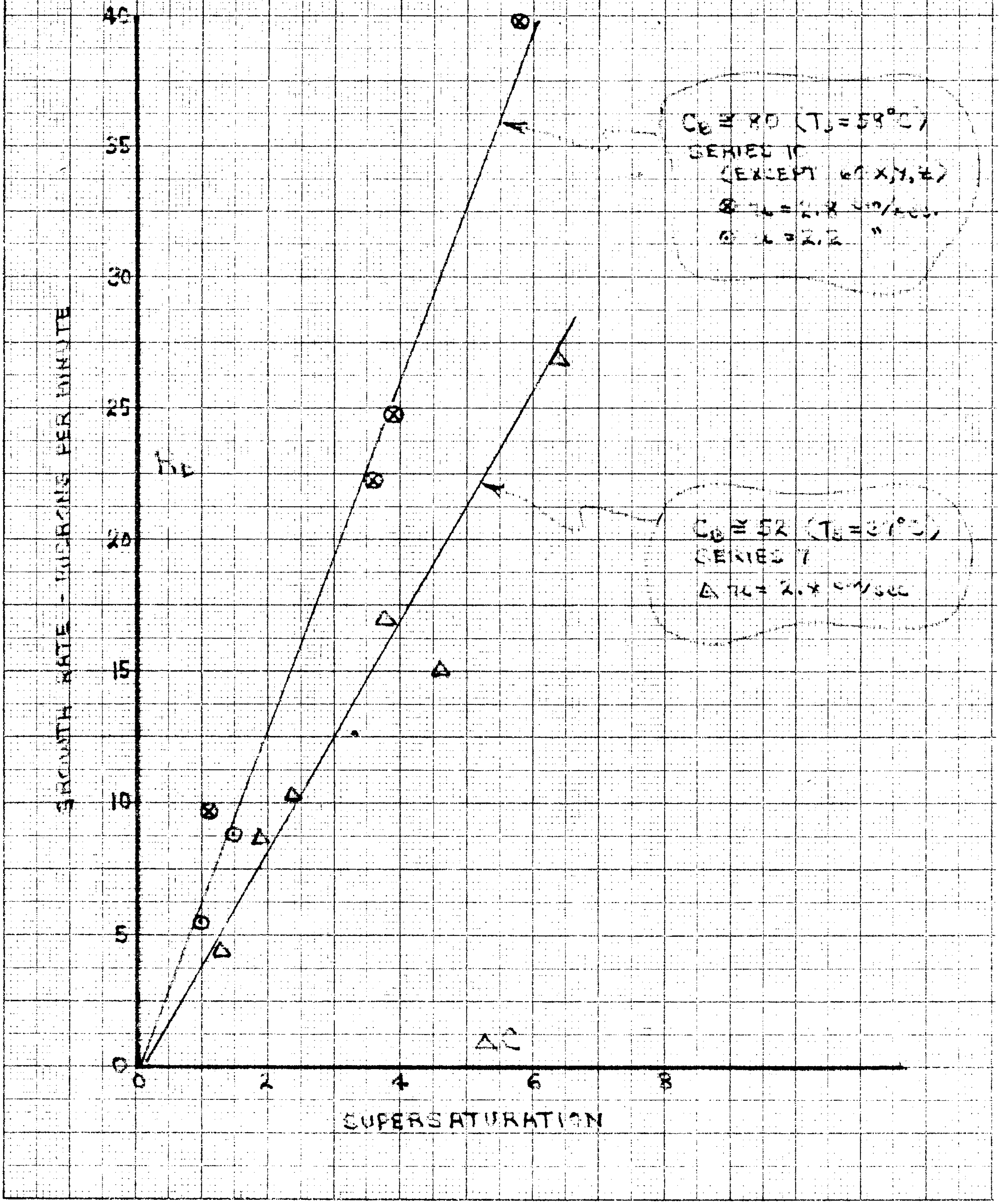

GROWTH RATE - MICRONS PER MINUTE
SUPERSATURATION
0
2
4
6
8
5
10
15
20
25
30
35
40

FIGURE V

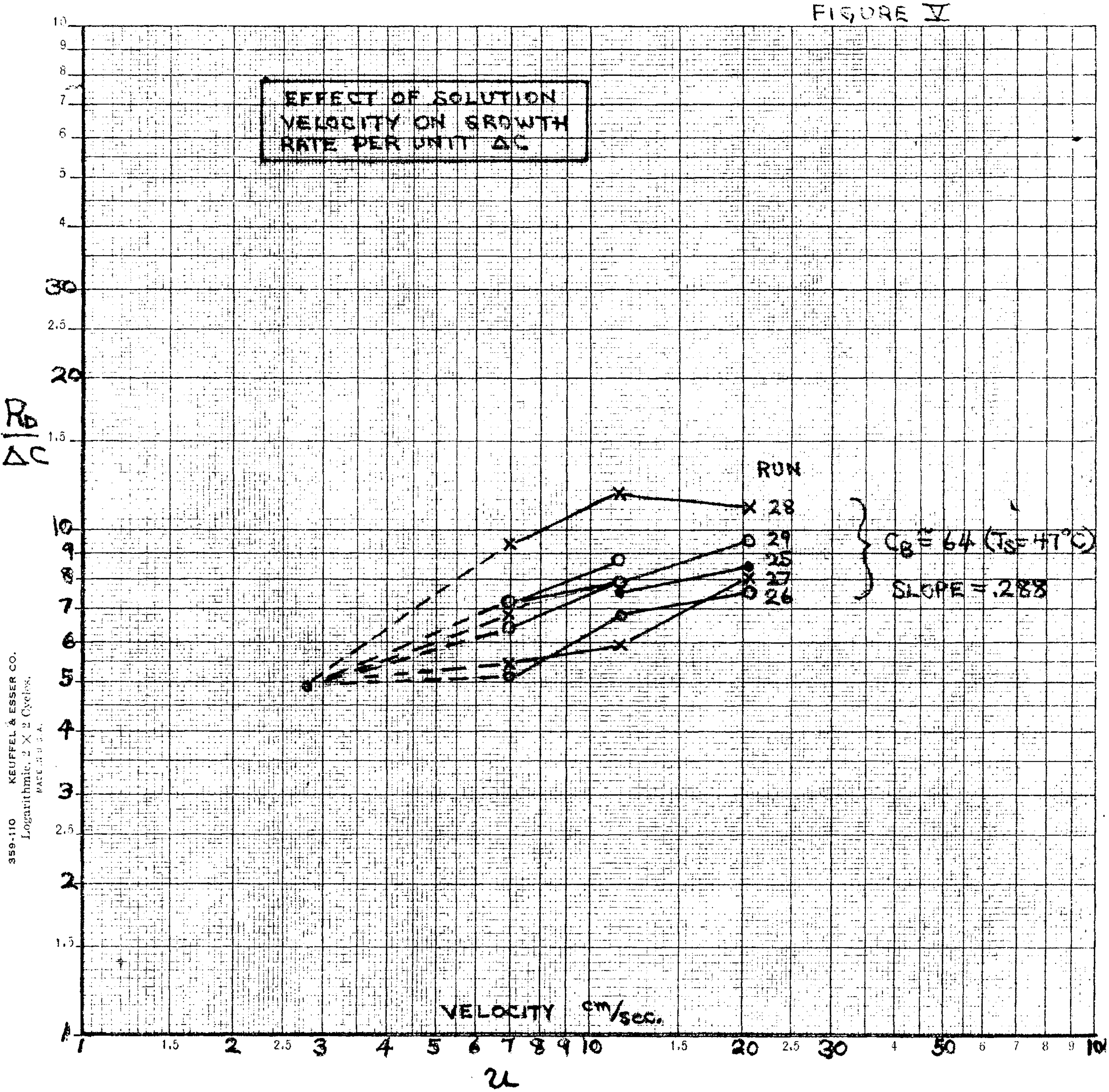
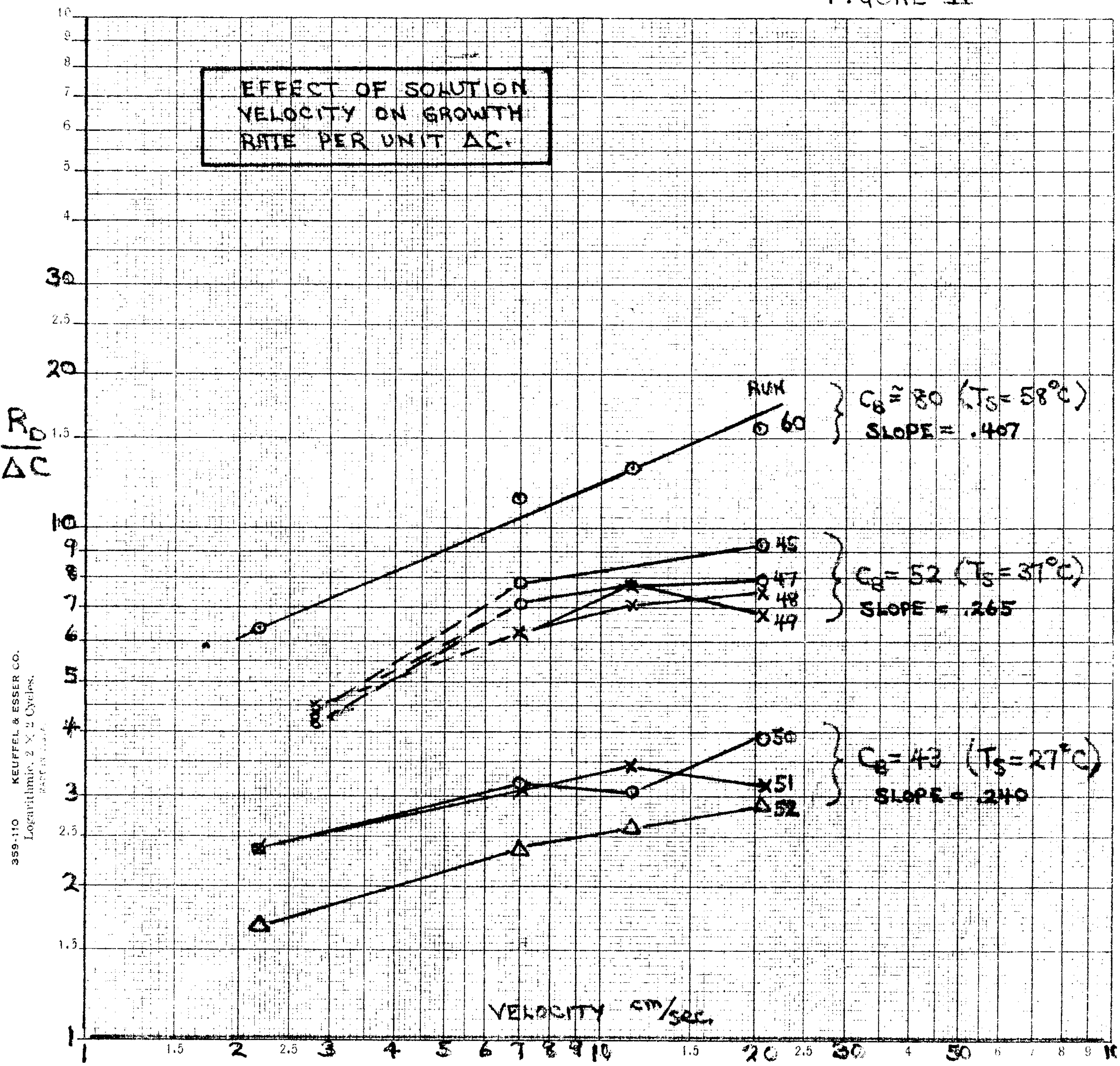

EFFECT OF SOLUTION VELOCITY ON GROWTH RATE PER UNIT ΔC
$\frac{R_D}{\Delta C}$
RUN
28
29
25
27
26
$C_B = 64$ ($T_S = 47°C$)
SLOPE = .288
VELOCITY cm/sec.
u
KEUFFEL & ESSER CO.
359-110 Logarithmic, 2 X 2 Cycles.

FIGURE VI


EFFECT OF SOLUTION VELOCITY ON GROWTH RATE PER UNIT ΔC.
RUN
60
$C_B \approx 80$ ($T_S = 58°C$)
SLOPE = .407
45
47
48
49
$C_B = 52$ ($T_S = 37°C$)
SLOPE = .265
50
51
52
$C_B = 43$ ($T_S = 27°C$)
SLOPE = .240
$R_D / \Delta C$
VELOCITY cm/sec.
KEUFFEL & ESSER CO.
359-110
Logarithmic, 2 X 2 Cycles.

2

FIGURE VII

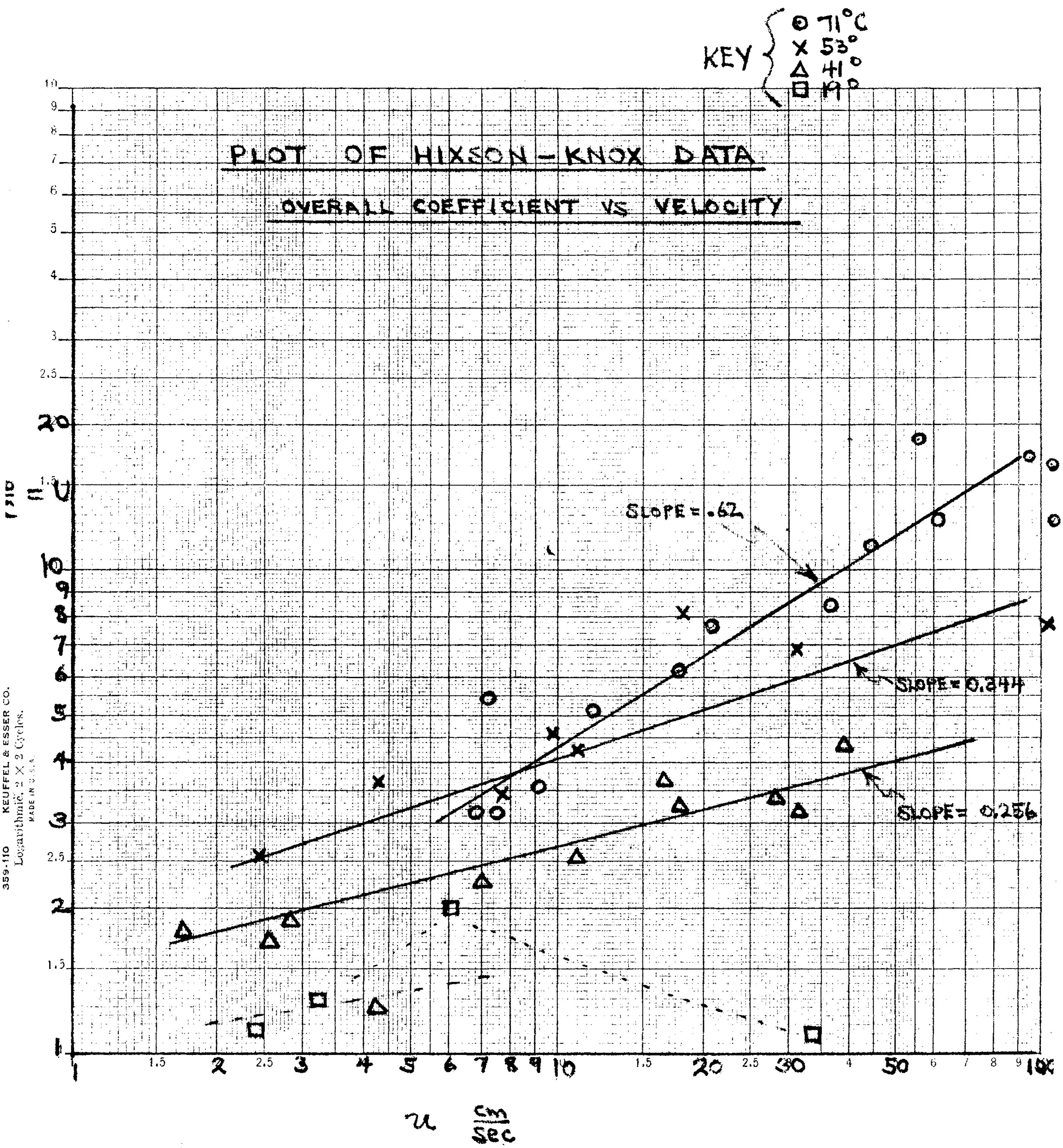

KEY
⊙ 71°C
× 53°
△ 41°
□ 19°
PLOT OF HIXSON-KNOX DATA
OVERALL COEFFICIENT VS VELOCITY
SLOPE = .62
SLOPE = 0.244
SLOPE = 0.256
U
u cm/sec
359-110 KEUFFEL & ESSER CO.
Logarithmic, 2 X 2 Cycles.
MADE IN U.S.A.

FIGURE VIII

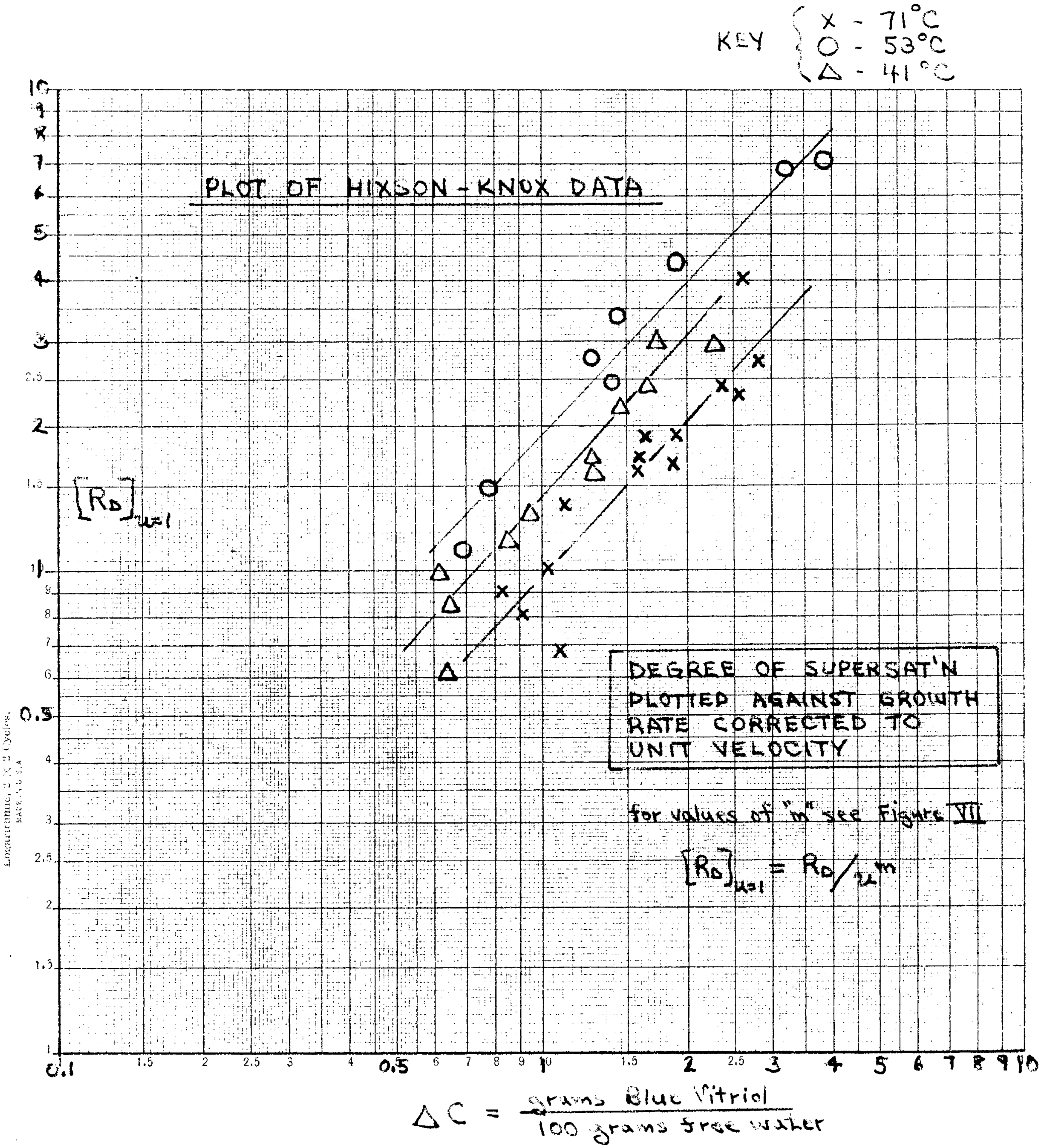

KEY
X - 71°C
O - 53°C
Δ - 41°C
PLOT OF HIXSON - KNOX DATA
DEGREE OF SUPERSAT'N PLOTTED AGAINST GROWTH RATE CORRECTED TO UNIT VELOCITY
for values of "m" see Figure VII
$[R_D]_{u=1} = R_D / u^m$
$[R_D]_{u=1}$
$\Delta C = \frac{\text{grams Blue Vitriol}}{\text{100 grams free water}}$

FIGURE IX

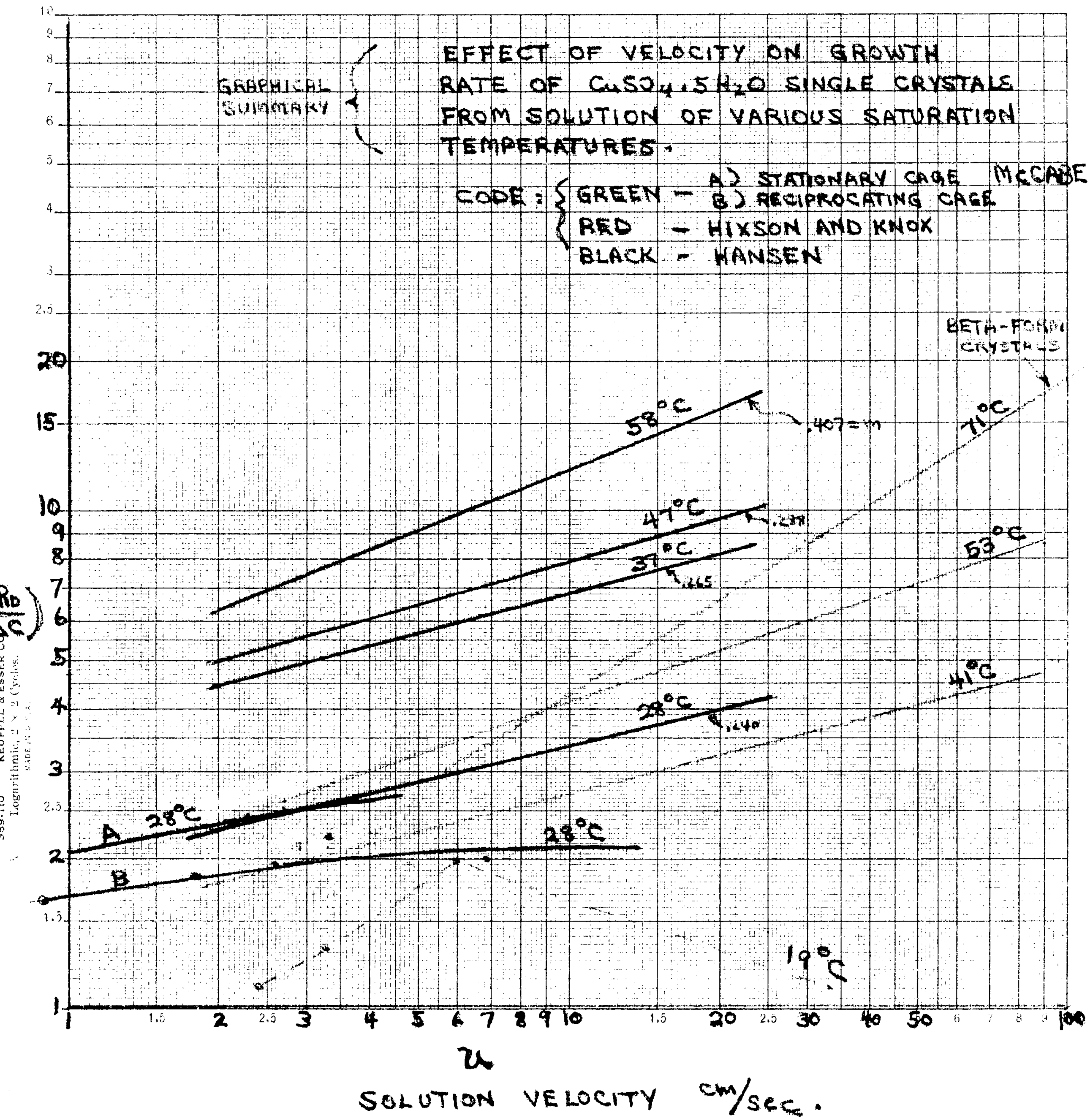
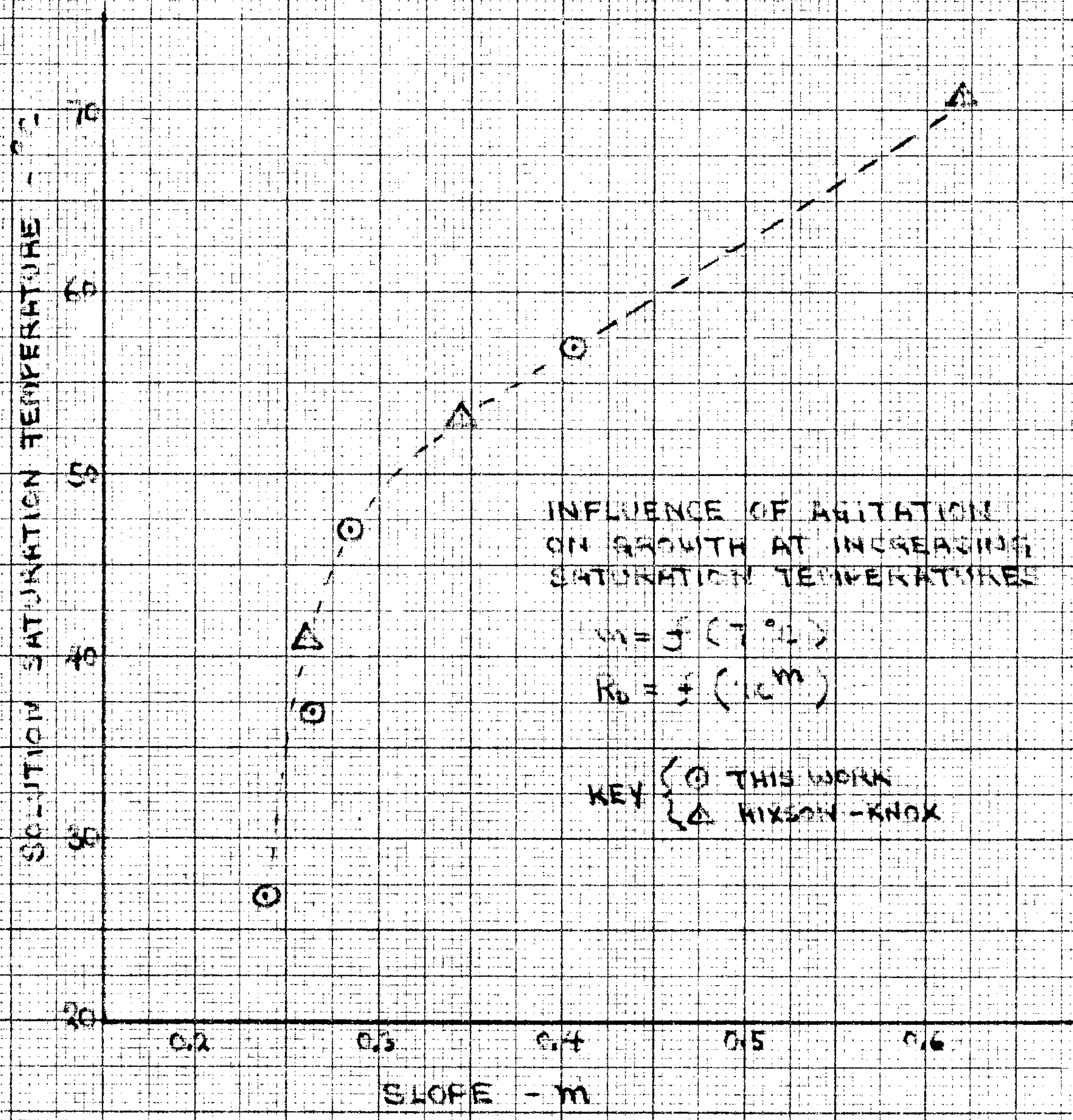
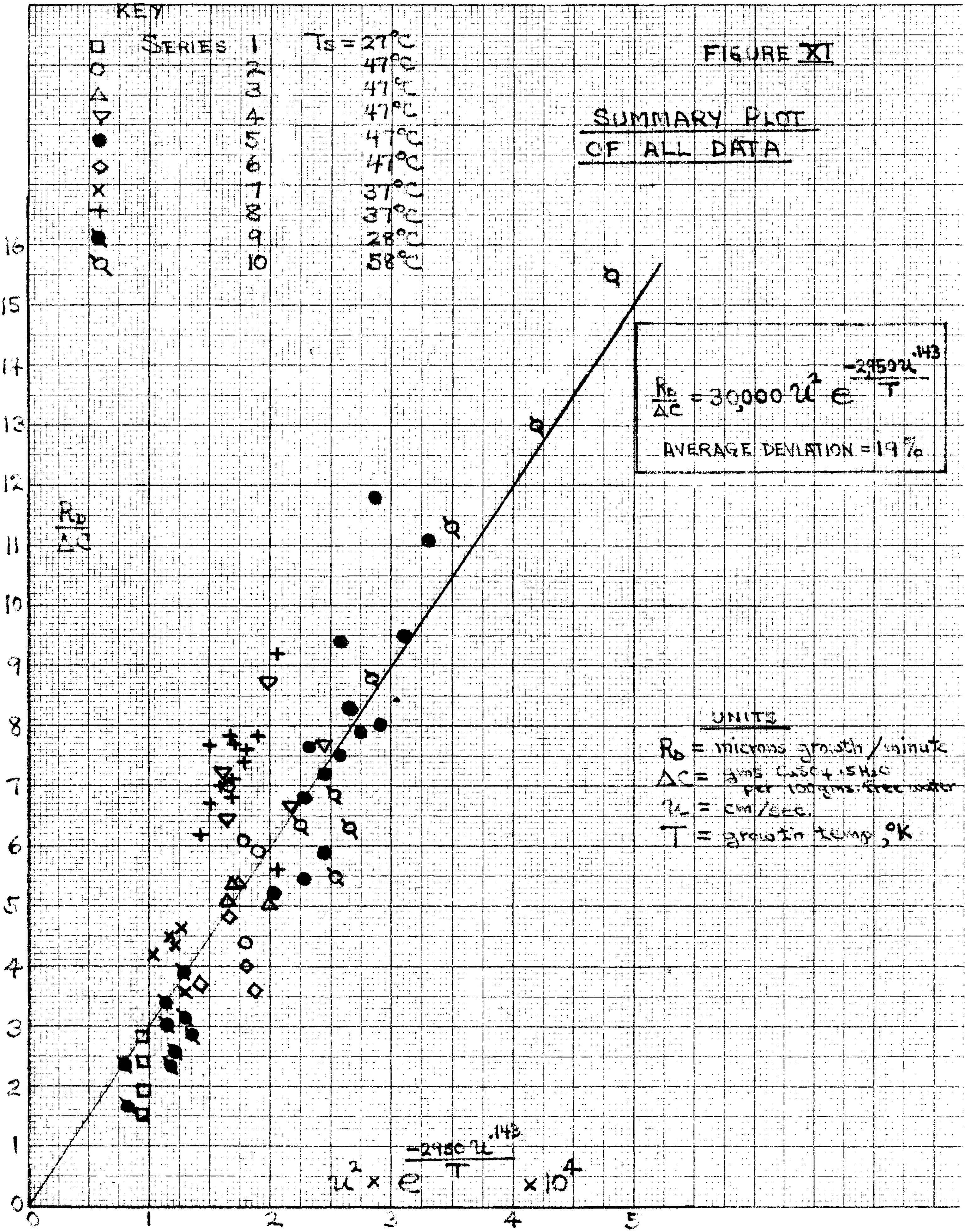

EFFECT OF VELOCITY ON GROWTH RATE OF $CuSO_4 \cdot 5H_2O$ SINGLE CRYSTALS FROM SOLUTION OF VARIOUS SATURATION TEMPERATURES.
GRAPHICAL SUMMARY
CODE: GREEN – A) STATIONARY CAGE B) RECIPROCATING CAGE McCABE
RED – HIXSON AND KNOX
BLACK – HANSEN
BETH-FORM CRYSTALS
58°C
.407 = n
47°C
.238
37°C
.265
28°C
.240
71°C
53°C
41°C
A 28°C
B
28°C
19°C
u
SOLUTION VELOCITY cm/sec.
Rb / ΔC
Logarithmic, 2 × 2 Cycles.
KEUFFEL & ESSER CO.

FIGURE X



NOTE: This curve implies that the surface orientation reaction is predominant below 50°C. At higher temperatures the growth process becomes diffusion-controlling — or perhaps a transitional phase change and emergence of the little-known "beta" form crystal occurs. However, no change in crystal habit was noted in this work — or evidently in Hixson's work either.


KEY
□ SERIES 1 Ts = 27°C
○ 2 47°C
△ 3 47°C
▽ 4 47°C
● 5 47°C
◇ 6 47°C
× 7 37°C
+ 8 37°C
9 28°C
10 58°C
FIGURE XI
SUMMARY PLOT OF ALL DATA
$\frac{R_D}{\Delta C} = 30{,}000\, u^2 e^{\frac{-2950 u^{.143}}{T}}$
AVERAGE DEVIATION = 19%
UNITS
R_D = microns growth / minute
ΔC = gms $CuSO_4 \cdot 5H_2O$ per 100 gms. free water
u = cm/sec.
T = growth temp, °K
$\frac{R_D}{\Delta C}$
$u^2 \times e^{\frac{-2950 u^{.143}}{T}} \times 10^4$
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

DISCUSSION - EXPERIMENTAL METHOD

Several weeks work were required to become familiar with the apparatus. Difficulties encountered and problems to be worked out were as follows:

1. Obtaining close control of cooling water temperature.

2. Obtaining close control of heater input.

3. Handling of crystals and sampling - from a fluidized bed.

4. Avoidance of nucleii formation and freeze-up of the apparatus.

5. Find a sufficiently accurate method for measurement of solution concentration.

6. Obtain accurate data on solubility of copper sulphate.

7. Use of the rheostat for varying the solution velocity gave only a narrow range of velocities.

8. Obtaining a wide range of ΔC.

9. Measurement of crystal growth.

For the first fifteen runs, difficulty was encountered in keeping the cooling water constant ($\pm$ 1/2° C.). This was remedied by using a large bucket as a reservoir. Good temperature control was obtained by adding a quantity of cold water about every ten minutes.

To obtain better heat control, the electric heater was graduated with ten divisions. This enabled the writer to reach and duplicate desired operating conditions in a short amount of time.

Because of the multiplicity of variables in crystal growth fluid beds and due to experimental difficulties, the writer decided to concentrate on single crystals rather than a large quantity of crystals. Although the apparatus was designed by a local equipment company for fluid-bed crystal experiments, the writer found it adaptable for single crystal work. This simplified the operation of the apparatus and enabled the writer to collect considerable data in a relatively short amount of time. Single crystals could be grown under steady state conditions, for several hours if necessary. With only 3 or 4 crystals in the system, nucleation was inhibited. For the same reason, no filter or porous plate was needed.

Any nucleii formed in the sub-cooled portion of the apparatus were swept into the dissolver, wherein they dissolved under controlled unsaturation conditions. It was found that a retention time of two minutes, moderate agitation, and a solution kept one or two degrees above the saturation point would rapidly redissolve the invisible nucleii formed during the course of a run.

Solution concentration was measured by a standardized hydrometer. Periodic readings throughout a run checked consistently to the nearest 0.1° Be.

Using the solubility data from the International Critical Tables (stated to be only accurate to ± 2%) the writer found that dissolution or shrinkage of the crystals occurred under supposedly supersaturated conditions. Solubility data from Seidell "Solubilities of Inorganic Compounds" when plotted, gave a curve which did not coincide with ICT. The writer then decided to obtain solubility data using the apparatus in figure #5.

The data obtained was found to lie on a smooth curve. The validity of the curve was then checked by placing crystals under saturation conditions in the crystallizer for a length of time (1 - 30 minutes). No change in weight resulted.

Variation of the speed of the recycle solution pump (220 volts D.C.) permitted a limited range of solution velocities (see Fig. II). In addition, the pump would stall at low speeds. To obtain a velocity spread, the writer hooked up several tubes in series. This had the additional advantage in that several crystals could be grown simultaneously without a source of ΔC error, since the temperature drop across the series of tubes was found to be negligible when the system was in equilibrium.

The writer feels that Hixson's range of ΔC was limited because of the presence of a bed of crystals and a filter in his apparatus. A filter capable of removing microscopic crystal nucleii would have a very large pressure drop. Function of the dissolver has been previously described.

The writer felt that the simplest and most rapid way to measure crystal growth was with the use of an analytical balance. Linear growth could most easily be expressed as the difference between the cube roots of the final and initial weights $(W_2^{1/3} - W_1^{1/3})$. This form of expression cannot be visualized, however, nor compared with the work of others.

The writer chose McCabe's units because they were simple. In order to compare with Hixson, the writer converted growth units first to $\frac{W_2 - W_1}{A\theta} = G$ and then to R_D.

DISCUSSION - GENERAL

According to the International Critical Tables, the presence of a "beta" form of copper sulphate occurs at about 60°C. This temperature is above the range (27°-58°C) studied in this work. The data of Hixson-Knox show a wider scatter above this temperature (see Figure VII).

Growth rates obtained agree with that of McCabe's cage experiments, but are about twice as high as Hixson's. This may be due partly to a difference in assumed crystal geometry, and also to an edge-effect. Hixson used crystals about one half inch in size as compared with one-eighth inch used by the writer. The quantitative effects of solution velocity were found to agree with both McCabe's and Hixson's findings.

This writer is unable to agree with Hixson's complex correlation for several reasons:

1. Growth rate was found to be independent of particle size - this would not be true in a fluidized bed of crystals where settling velocity comes into play. In any case, this writer feels that the D term in Re should be the tube diameter. A modified Re would be needed to correlate fluid-bed studies - rather than modify the D term, this writer would attempt to modify the u or velocity value. This modified velocity could probably be obtained by deriving some relation involving Stokes Law, settling velocity etc.

2. A plot of growth rate vs. Reynolds number cannot give parallel curves on log-log paper because the effect of velocity varies with solution concentration (or temperature).

3. Diffusivity data is questionable.

4. Hixson assumed the viscosity to be constant regardless of the effect of sub-cooling for a given saturation temperature. Application of the log μ vs log Absolute temperature rule for obtaining viscosities, indicates a 10% increase in the viscosity value for five degrees of sub cooling.

Factors to be considered for future work on the study of crystal growth should include:

1. Correlation with activities or degree of ionization - compare with use of concentration values.

2. The significance of a "Critical" crystal size above which perfect crystals cannot or are difficult to grow.

3. The effect and mechanism of pH on growth.

The writer feels that discrepancies and the scatter of data in crystal growth work are not due to the errors involved in measurement, but due to the crystal itself. The cause may lie in a film of dehydrated material or dust on the crystal service, the presence of imperfections on the surface, etc.

A possible means of overcoming this is by preparing the crystal - perhaps a short submersion in slightly under-saturation solution. The time of growth may be a factor. A time-growth curve would clarify this.

The data from this work, though greater in quantity, is probably inferior to Hixsons from the standpoint of scatter, particularly in the early runs.

Data on the low concentration ($T_s = 27°$) runs is insufficient to confirm the linear effect of ΔC, or to disprove McCabe's equation (using an agitator, tank, large quantity of seed)

$$R_L = f(\Delta C\ 1.8)$$

NOMENCLATURE

C_R = solution concentration gm $CuSO_4 \cdot 5H_2O$ per 100 gm. free water

W = weight crystal - mgm

V = volume crystal - mm^3

A = area crystal - mm^2

θ = time - minutes

R_D = $\frac{\Delta D}{\theta}$; $R_L = \frac{\Delta L}{\theta}$

D = diameter of sphere having same area as crystal - μ

L = square root of long x short sides of crystal - μ

T_2 = crystal growth temperature °C

T_S = saturation temp. of solution °C.

T = absolute temperature °K.

u = velocity cm./sec.

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