THE VELOCITY OF CRYSTALLISATION OF SUCROSE.

-by-

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Abstract of Thesis to be Submitted
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"The Velocity of Crystallisation of Sucrose".

A critical summary is given of the literature on velocity of crystallisation of sucrose and of other substances from solution, and the necessity for a more precise experimental method pointed out.

The development of a new method for studying the velocity of crystallisation of sucrose is described, which enables the experimental conditions of supersaturation of solution and rate of flow of solution relative to the crystal to be more accurately defined than hitherto.

Methods are given for the measurement of the rate of growth of fourteen individual faces of the sucrose crystal in a normal direction.

The results obtained with the new methods are divided into two sections, dealing with the effect on crystallisation velocity of:

1) The rate of flow of solution relative to the crystal.
2) The supersaturation and temperature of the solution.

The bearing of these results on the problem of elucidation of the mechanism of the crystallisation process is discussed.

A new method for the determination of the solubility of sucrose at various temperatures is also described, and solubility figures given which indicate that the previously accepted solubility table for sucrose in pure solution is appreciably in error.

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PART 1.

THE VELOCITY OF CRYSTALLISATION OF SUCROSE.

INTRODUCTION.

Although the development of X-ray methods has resulted in a great increase in the knowledge of crystal structures, the subject of crystal growth has received relatively little attention, and the mechanism of the formation of the crystal lattice is still largely speculative.

The growth of crystals from one component systems such as vapours and melts has been studied experimentally to a certain extent, and theoretical contributions have been made in recent years by Kossel, Stranski and others. Although much scattered work has been published on the subject of crystallisation from solution, no conclusive evidence has so far been offered to explain the mechanism of the process. The problem is of interest both from the point of view of crystallography and from the more general standpoint of heterogeneous reaction kinetics in solution, and in addition is of technical importance in the Chemical industry.

In undertaking the present work on sucrose, the technical view-point was partly in mind, as the sugar industry is one in which the crystallisation process is of outstanding importance.

The process of crystallisation from solution in general may be divided into two parts:

(1) The formation of nuclei

(2) The growth of nuclei to macroscopic crystals.

In addition, the effect of impurities on crystallisation is another distinct field.

The present work has been confined to the study of the growth of macroscopic crystals from pure solution; the problem of nuclear formation, and the effect of impurities have not been considered.

I SUMMARY OF PREVIOUS INVESTIGATIONS.

In the following summary no attempt has been made to include all the papers which have been read, as many of them differ only slightly as regards experimental technique and conclusions drawn, and reference will only be made to those which have been judged to be the more important contributions.

Although a considerable literature has resulted from the study of the velocity of crystallisation from melts (the work of Tammann (1) being noteworthy) this will not be dealt with as the experimental and theoretical sides of this problem have only slight bearing on crystallisation from solutions.

The following summary is divided into two sections, the first dealing with sucrose, and the second with other substances.

(1) Sucrose

Practically the only work of any degree of completeness on the velocity of crystallisation in pure solution has been carried out by Kucharenko and collaborators at the Institute of Sugar Technology at Kiev. The original papers are in Russian but translations and summaries are available in various French and American journals.

Kucharenko's experimental method (2) was to introduce a large crystal of sucrose into a solution of known supersaturation and temperature in a stoppered bottle, and rotate for a definite time in a thermostat. The weight of sucrose crystallising during the period was found by weighing the crystal before and after growth.

In the calculation of the velocity of crystallisation under given conditions of supersaturation and temperature it was assumed that the rate of deposition of sucrose was proportional to the surface area of the crystal, and to avoid having to measure surface areas in each experiment preliminary determinations of the weight/surface area relationships were made.

For solids of similar external form, the surface area will be proportional to the 2/3 power of the weight.

i.e. $$S = K M^{2/3} \qquad (1)$$

Kucharenko, using very large crystals of sucrose weighing from 150 to 2500 gms. measured surface areas and evaluated K. 13 crystals were measured, giving a mean value for K of 4.12 ± 0.05, and this value was used throughout to calculate surface areas of the crystals employed in the velocity of crystallisation experiments.

Thus, assuming that the rate of increase in the weight of a crystal is proportional to surface area,

$$\frac{dM}{dt} = \alpha S$$

Where α is a constant depending on the solution.

Substituting for S from (1)

$$\frac{dM}{dt} = \alpha K M^{2/3} \qquad (2)$$

which on integration gives

$$M_2^{\frac{1}{3}} - M_1^{\frac{1}{3}} = \frac{1}{3} \alpha K t \qquad (3)$$

Where M_1 = initial weight of crystal
and M_2 = weight of crystal after time t.

In the calculation of crystallisation velocities Kucharenko took the mean value for the surface area, given by

$$K \left(\frac{M_1 + M_2}{2}\right)^{2/3} ,$$

and used the formula

$$M_2 - M_1 = \alpha K t \left(\frac{M_1 + M_2}{2}\right)^{2/3} \qquad (4)$$

The difference between the values of α calculated from equations (3) and (4) is small if $\frac{M_2}{M_1}$ is little different from unity, and as large crystals were used for the experiments, equation (4) is sufficiently exact. Crystallisation velocities were expressed as mgms. sucrose crystallised per sq. metre crystal surface per minute and experiments were carried out at temperatures ranging from 0° to 70° C. at various supersaturations at each temperature. The results reported by Kucharenko will be compared with the writer's values in a later section.

Savinov (3) showed that the rate of movement of solution relative to the crystal influenced the velocity of crystallisation, by mounting crystals between needle points on the arms of a rotating stirrer. It was found that velocity of crystallisation increased with increasing speed of rotation up to a maximum which was about six times the value determined by Kucharenko.

Briedveld and Waterman (4) introduced slight modifications of Kucharenko's technique and found velocities less than half those of Kucharenko under comparable conditions of supersaturation and temperature of solution.

A number of workers have derived more or less empirical equations for representing Kucharenko's results. Kirof (5) de Vries (6), and Siline (7) may be mentioned. None of these equations have much theoretical significance, and do not assist to any extent in the elucidation of the mechanism of the process.

(2) Substances other than Sucrose.

Reference should first be made to the work of Noyes and Whitney (8) on the velocity of dissolution of substances such as benzoic acid in water, as their ideas have frequently been applied to the case of crystallisation. The substance to be investigated was compressed into a cylinder, and this rotated about its axis in water. Concentration changes were followed analytically.

It was found that the velocity of dissolution of the solid followed an apparently monomolecular law :

$$\frac{dx}{dt} = k \ (S - x)$$

where S = solubility of the solid,

and x = the concentration in the bulk of solution at time t.

The rate of dissolution being proportional to the difference between the saturated and observed concentration, it was suggested by them that a saturated layer is formed at the surface of the solid. The velocity observed is then the velocity with which solute molecules can diffuse into the liquid.

Brunner and Tolloczko (9) substantiated this conclusion by examining the rate of dissolution of various substances in water. The velocity was found to be proportional to the area (A) of the surface

i.e. $\frac{dx}{dt} = K A (S - x)$.

Since the reaction was unimolecular throughout the complete process, it appeared that the effective area remained constant although the actual surface of the solid became eroded.

This theory was generallised by Nernst (10) to include heterogeneous reactions in general and crystallisation in particular. Nernsts' theory has aroused much discussion and a number of investigations have been undertaken in order to test its applicability.

Brunner (9) and others claimed to have established its correctness, while Wildermann (11) criticised it adversely, pointing out that the unimolecular behaviour may be explained in other ways.

The Nernst theory may be described as follows :

Consider a solution of volume V litres containing C gm. molecules of solute per litre. Between the solution and the crystal surface (area A) exists a layer of thickness d, across which diffusion must take place. The amount of solute reaching the surface in time dt is ds, this reducing the concentration of solution by an amount $\frac{ds}{V}$

By Fick's diffusion law;

$$\frac{ds}{dt} = DA\frac{dc}{dx}$$

where $\frac{dc}{dx}$ = concentration gradient .

Hence $\frac{dc}{dt} = \frac{1}{V}\,\frac{ds}{dt} = \frac{DA}{V}.\,\frac{dc}{dx}$

The concentration gradient being $\frac{c - C_o}{d}$ we have:

$$\frac{dc}{dt} = \frac{DA}{Vd}\cdot(C - C_o)$$

and $k_{unit} = \frac{dc}{dt}\cdot\frac{1}{C-C_o} = \frac{DA}{Vd}$

Thus for a surface area of 1 cm^2. and a volume of 1 litre,

$$d = \frac{D}{k},$$

an equation which has been used by Brunner to calculate the thickness of the saturated layer. For a number of reactions, values for d were of the order of 3×10^{-3} cms.

It was found that stirring increased the velocity of reaction, the velocity rising to a maximum with increasing stirring speed. This was explained in terms of the theory by assuming that the thickness of the layer was reduced by the more rapid motion, down to a limiting value.

One of the difficulties of the theory is that it does not take into account the possibility of varying speeds of reaction on the surface; it seems extremely probable that differences do in fact occur, and that the Nernst theory is only a special case where the reaction at the surface is fast compared with diffusion velocity. Furthermore, applying the theory to crystal growth from solution, crystals under equal external conditions would grow into spheres. There is nothing in the diffusion process to explain the regularity of crystal growth, and it is impossible to see from the standpoint of the theory only how the predominantly regular crystal form comes about.

Marc (12) in a long series of papers, criticised the Nernst theory and found that it did not hold in all cases. In some of the cases studied, crystallisation rate was found to be proportional to some power of the supersaturation. His results led him to the conclusion that an adsorbed layer was formed on the crystal faces, as an initial rapid fall in supersaturation was observed when a quantity of fine crystals was stirred in a supersaturated solution.

Considering the crystallisation process from the point of view of crystal structure, various attempts have been made to explain the differing growth rates of crystal faces. One of the earliest suggestions was that the growth rate depended on the "reticular density" of the face, a view supported by Wulff (13) who carried out experiments on the growth of alum crystals.

The knowledge of the X-ray structures of ionic crystals has been utilised in endeavours to explain the differing rates of the faces. The magnitude and nature of the forces acting at a crystal surface is still very largely unknown however, and actual calculations have been made in only very few cases, such as by Lennard-Jones (14) who took the (100) face of NaCI as being most susceptible to calculation. With molecular crystals the problem is even more difficult and practically nothing is known in this field.

Regarding the experimental methods which have been used for the study of crystallisation from solution, the following may be mentioned:

Marc (12) in his work on various salts, followed the course of the crystallisation by the periodic analysis of the solution. Conductivity methods were also employed. A dipping refractometer was similarly used by Jenkins (15) for following changes in concentration.

Methods involving single crystals have been employed by Andrejev (16) and Campbell (17) who recorded increase in weight. The method of Wullff (13) was improved by Bentivoglio (18) who attached crystals rigidly to a holder, and measured the vertical displacements of the faces by means of a microscope. Müller (19) using rock salt, made artificial crystals and allowed these to grow in solution. The boundary between the initial crystal and the crystallised layer could be distinguished under a microscope and the thickness of layer measured.

Photographic, including cinematographic, methods have been used by Richards and Archibald (20) and Franco (21) and co-workers.

In few of the methods which have been reported for the study of crystallisation velocity does there appear to have been sufficient control of the experimental conditions, and many of the results are of a purely empirical nature.

II EXPERIMENTAL.

(1) Introduction.

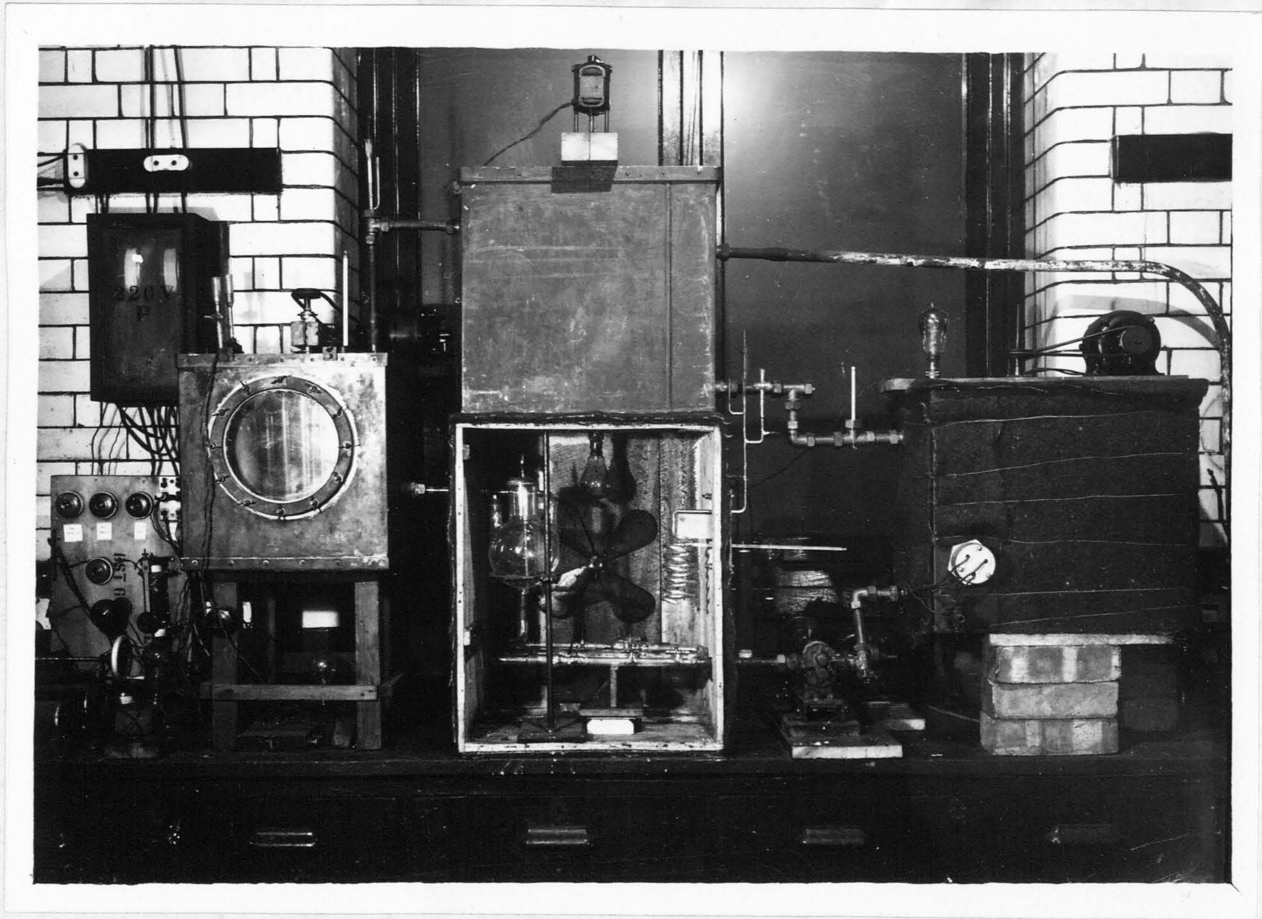
The general requirements for a method for studying crystallisation velocity from solution appear to be:

1. A method of controlling the degree of supersaturation of the solution (this involving both concentration and temperature)
2. A means of varying the rate of flow of solution relative to the crystal.
3. A method of measuring the amount of substance crystallised.

The experimental method finally developed consists essentially in supporting a sucrose crystal about 5 mms. long in a cylindrical glass cell and pumping a solution of known supersaturation and temperature past it at a given rate. Recirculation of solution is necessary as the experiment has to continue for some hours. If this were carried out at constant temperature, spontaneous crystallisation throughout the bulk of solution would rapidly occur. It was found however that this could be prevented by inserting heating and cooling coils in the circulating system so that once ~~and~~ in every cycle the solution is heated to above its saturation temperature and then cooled again before re-entering the cell. As is well known a supersaturated solution may in general be kept for some little time if crystals are excluded. This is so to quite a marked extent with sucrose, and thus after the solution has been undersaturated in the heating coil, it may be circulated through the remainder of the circuit and past the crystal without spontaneous crystallisation taking place. This principle of circulation with heating and cooling has proved very useful as it has enabled solutions of fairly high supersaturation to be investigated. Furthermore, since the volume of solution is very large compared with the amount of sucrose crystallising, the concentration of solution remains virtually unchanged throughout an experiment.

To investigate the effect of rate of flow of solution past the crystal on ~~and~~ crystallisation velocity, cells of different diameter were connected in series so that rate of flow could be altered under otherwise strictly comparable conditions.

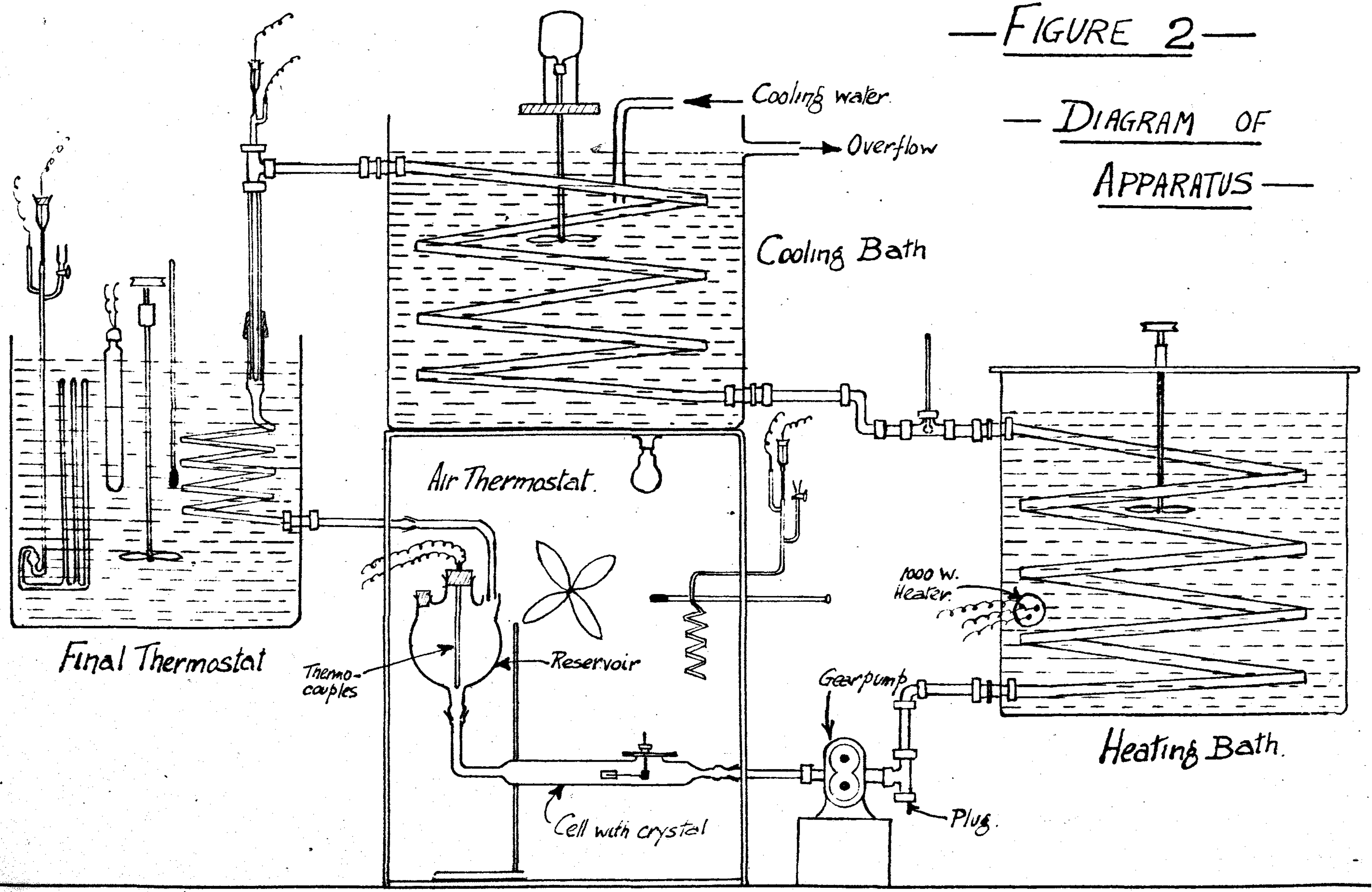
As regards measurement of the crystals a method was found by which the growth rates of individual faces of the



— FIGURE 1 —

—FIGURE 2—

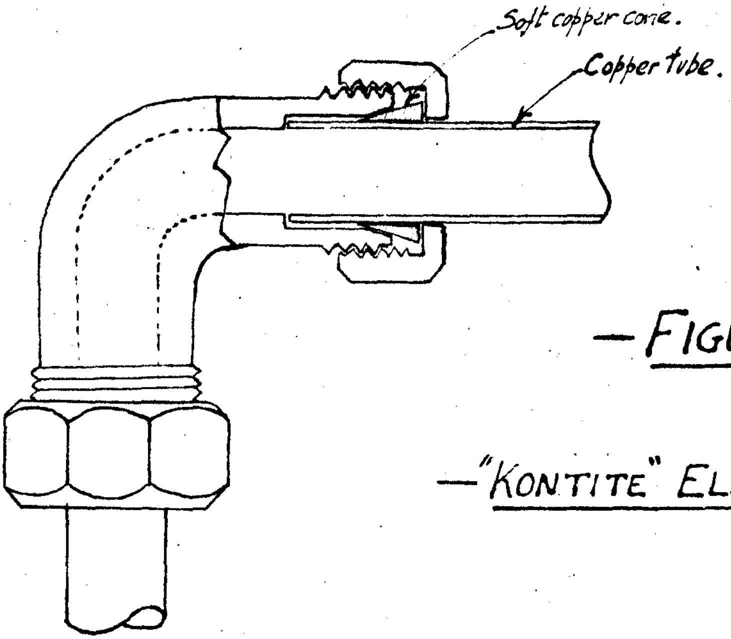
— DIAGRAM OF APPARATUS —



coils of different diameters, connected in series, were used, but for the sake of simplicity only one has been shown in the diagram. The construction of the cells and crystal holders will be dealt with later. (see pp. 19a — 20).

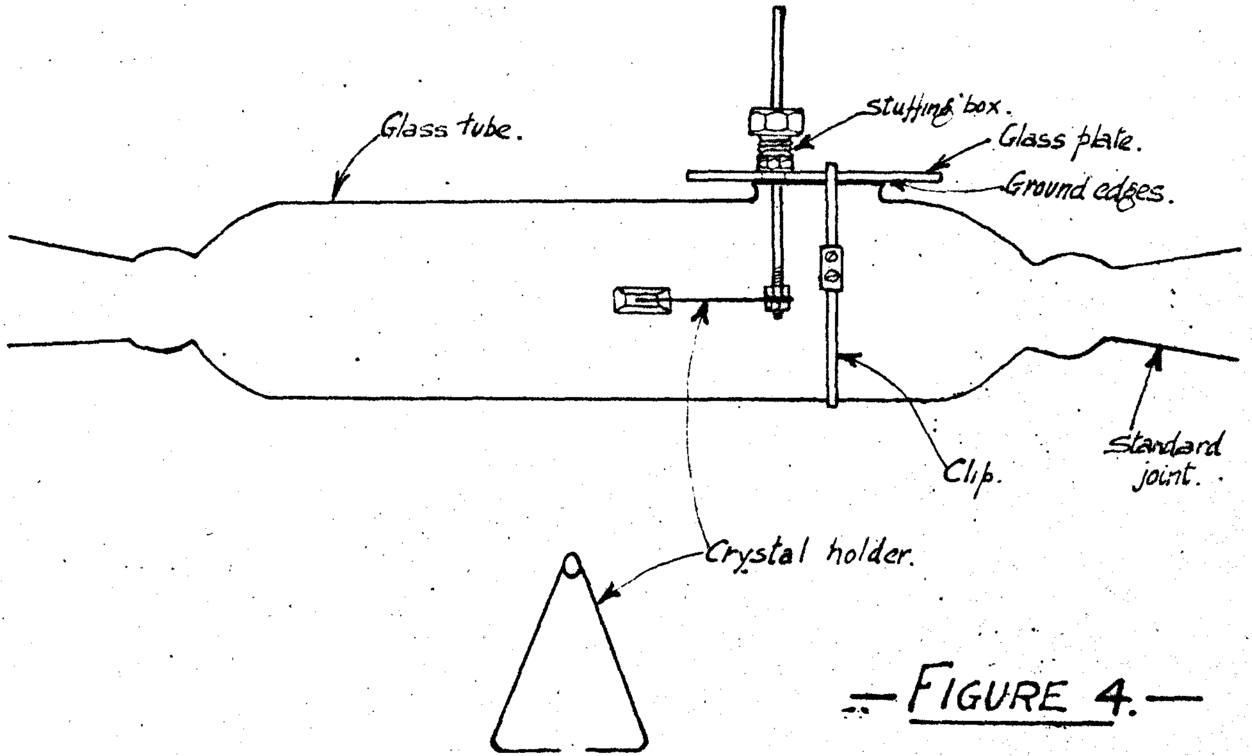
The supersaturated solution leaving the air thermostat to the right enters the intake side of a phosphor-bronze gear pump, direct coupled through suitable worm reduction gearing to a 1/4 H.P. induction motor, and is pumped through a copper coil 18' long of 3/4" x 18 S.W.G. tube arranged in the heating bath as shown. The bath is fitted with a 1000 W. immersion heater, and stirrer.

Standard brass "Kontite" fittings were used throughout the apparatus for connecting together the various component parts. A diagram of an elbow fitting is shown in Figure 3 to illustrate the method of attachment. The copper tube slides into the fitting and a joint is made by compressing a soft copper cone into the space between the tube and the outer tapered shoulder. This type of fitting has been found very convenient for the construction of the apparatus as a joint may be readily made and taken apart, and does not require threading or soldering of the tubes. They also lend considerable mechanical strength to the whole system. A junction through the wall of a water bath was made from two



— FIGURE 3 —

— "KONTITE" ELBOW FITTING. —



— FIGURE 4. —

— CONSTRUCTION OF CELL. —

straight couplings, one having a "Kontite" fitting at one end and a male gas thread at the other, and the second a "Kontite" and female gas thread. These were screwed together with washers on both sides of the wall of the bath.

To the outlet tube from the top of the heating bath is attached a T piece, the side arm being adapted as a stuffing box to take a thermometer. Originally a mercury regulator, connected through a relay to the immersion heater was inserted in the tube through a second stuffing box, in order to control automatically the temperature of the solution leaving the heating bath, but this was later found to be unnecessary as accurate temperature control was not necessary at this point. Adequate control may be effected by hand regulation of the heater.

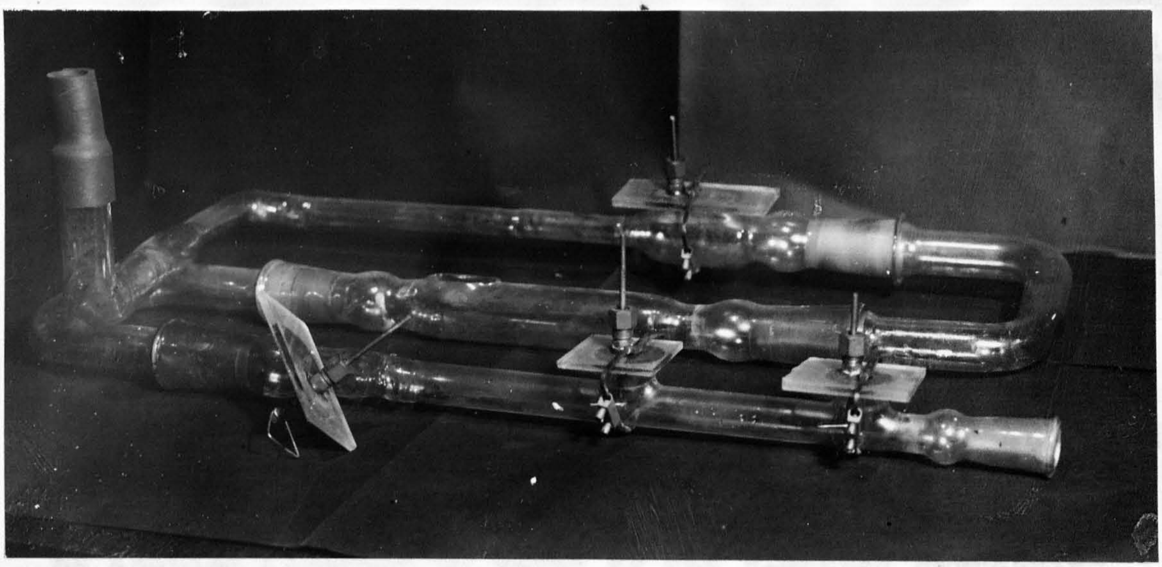
The solution now enters a similar copper coil in the first cooling bath, mounted on top of the air thermostat, the object of this bath being to cool the solution down to within about ± 0°5 of the required temperature. Two methods were used for the regulation of this bath. In the earlier part of the work a long thin mercury regulator was inserted through a stuffing box in the outlet tube from the bath and connected through a relay to an electromagnetic device for cutting off or turning on the cooling water to the bath. This was found to work satisfactorily and is the best method to employ when the rate of flow of solution through the coil is fairly high; i.e., when it is necessary to have the temperature of the water in the bath lower than the required exit temperature.

With the slower rates of flow used in the latter part of the work it was found more convenient and accurate to dispense with the outlet regulator and to have a toluene-mercury regulator in the cooling water bath itself to maintain the temperature of the bath at the required solution temperature. When using these lower rates of flow the length of cooling coil was sufficient to enable the solution temperature to fall to that of the water. Both methods enabled the temperature of the solution leaving the cooling bath to be regulated to well within ± 0°5 C.

After the first cooling bath, where the greater part of the necessary cooling of solution is done, a small coil in a final thermostat is provided to bring the temperature accurately to the required figure. This thermostat is maintained at the desired temperature with an accuracy of ± 0°02 C. The outlet tube from the final thermostat passes through the wall of the air thermostat and is bent to enter one of the side necks of the reservoir flask.

The details of construction of the glass cells containing the crystals are shown in Figures 4 and 5. When investigating the effect of rate of flow of solution on crystallisation velocity, three or sometimes four cells of different diameters were connected in series so that the solution could be made to flow past the crystals at different velocities under otherwise comparable conditions of concentration and temperature of solution. Figure 5 is a photograph of one assembly of three cells, the vertical tube to the left being connected to the reservoir, and the ground glass joint at the right, to the pump. The front cell has two openings to enable duplicate determinations to be made.

The construction of a cell and crystal holder is shown in detail in Figure 4. An oblong opening is made near one end of the tube and the edges ground to take a flat-ground glass plate drilled centrally and with a small brass stuffing box cemented in. The 3/32" brass spindle passing through the stuffing box has attached to it the crystal holder of stainless steel spring wire bent as shown and with the ends ground so that the crystal is held between sharp points. The cover plates are held in position by the clips shown in the photograph and diagram. When



— FIGURE 5 —

inserting a crystal in the cell the cover plate is pushed forward so that the crystal is clear of the opening and in the straight portion of the tube. After fixing the cover plate with the clip the crystal may be centered in the tube by adjustment of the spindle.

The method of construction of cells of small diameter can be seen from the photograph, Figure 5. The rear cell of the assembly consists of a straight length of narrow tubing, joined to a piece of about 28 mms. diameter, in which the oblong opening is made. The crystal holder is inserted and pushed forward to bring the crystal into the narrow tube.

Standard interchangeable ground glass joints were used for all cells so that cells of any desired diameter could be coupled together by means of the V-shaped connecting tubes.

No oil was used in the gear pump; the end bearings and rotors were cleaned initially with benzene to remove all traces. The copper coils were cleaned with HCI before use, and a number of times during the course of the work. Before commencing an experiment tap water was run through the system for about 24 hours and the coils finally washed with distilled water and allowed to drain through the plug shown in Figure 2. The glass cells and reservoir could be removed from the Air Thermostat for cleaning after every experiment.

(3) Solutions.

(a) Preparation. For the work on velocity of crystallisation a very high grade commercial refined sugar obtained from Messrs. Tate and Lyle Ltd. was employed. The sugar was of such high purity that no further purification beyond a filtration was thought to be necessary. The average percentages of impurities in the sugar used for the work were:

Reducing sugars	...	0.002%
Ash	...	0.003%

Filtration, however, was necessary in order to remove the fine particles of dust, hairs etc. that are unavoidably present in a commercial sugar; it was found that some of these invariably adhered to the crystals during the course of an experiment and caused distortion of the growing faces.

Two methods of preparation of solutions are possible:

(1) The solution may be made up reasonably dilute, filtered on a large Buchner funnel and then evaporated under vacuum to the required concentration, or

(2) A saturated solution may be prepared at a temperature higher than the required working temperature, and filtered hot.

The second method is only possible if some form of pressure filtration is used, as the high viscosity of concentrated sucrose solutions renders a vacuum filtration extremely slow.

As a small 6" square slate and frame filter press was available, the method of filtration of hot solutions was chosen. A filtering surface of 1.5 sq. ft. was employed, using three plates covered with fine weave flax cloth. The hand pump attached to the filter was found to be unsatisfactory on account of the violent fluctuations of pressure which occurred, and was discarded in favour of a pressure vessel attached to a compressed air supply. The pressure vessel was of mild steel, 8" diameter x 16" high, fitted with flange and cover. To the cover of the vessel were attached a pressure gauge, safety valve, a pipe for connecting to compressed air, and a stuffing box through which passed a pipe leading to the bottom of the vessel. A pressure hose connection was made from the latter to the inlet of the filter. Using compressed air supplied from a cylinder through a reducing valve, filtration pressures up to 70 lbs. per sq. in. (5 atmos.) could be applied in this manner.

In preparing a solution, the required amounts of sucrose and distilled water were measured out and partially dissolved at room temperature. The vessel containing the solution was then transferred to a water bath, the temperature raised to above the corresponding saturation temperature of the solution, and stirring continued until the sucrose was in solution.

After adding a small quantity of acid washed kieselguhr the solution was transferred to the pressure vessel, standing in a hot water bath to prevent undue cooling of solution, and pressure applied gradually up to a maximum of about 70 lbs. per sq. in. Discarding about the first 500 ccs. a very clear filtrate could be obtained. About 5 to 6 litres of supersaturated solution could be filtered in this manner in 30 minutes.

Because of the slow rate of spontaneous crystallisation of pure sucrose solutions, the filtered solution could be cooled to approximately the required temperature, transferred to the apparatus, and circulation started before crystallisation took place.

(b) Methods of Analysis.

SUCROSE: The solutions used were analysed polarimetrically for sucrose. The more rapid refractometric method was not employed for the analyses on which the calculations of degree of supersaturation were based, as the refractive index-concentration relationships of concentrated solutions are not known with as much certainty as are the polarimetric constants. Refractometers were used, however, in the preliminary determinations of approximate concentrations.

A Hilger polarimeter, reading to $0\overset{\circ}{.}01$ was used for the work, illumination being the Sodium D line from an Osram Sodium vapour lamp.

For the specific rotation of sucrose, the value determined by Bates and Jackson (22) at a concentration of 26.016 gms. per 100 ccs. was used, namely:

$$[\alpha]^{20^{\circ}}_{\lambda=5892.5\,\text{Å}} = 66\overset{\circ}{.}529$$

In making up the solutions for reading in the polarimeter, approximately the required amount of supersaturated solution was transferred to a tared 100 cc. flask and the flask stoppered and weighed. The concentration of the resultant solution in general differed somewhat from

26 gms/100 ccs., and to correct for change in specific rotation the formula of Landolt was used :

$$[\alpha]^{20}_{\lambda=5892.5\,\text{Å}} = 66.435 + 0.00870\,C - 0.000235\,C^2$$

Where C = concentration in gms/100 ccs.

This formula, which was based on earlier determinations of the specific rotation gives a value of 66.502 at a concentration of 26.016 gms/100 ccs., i.e., 0.027 different from Bates and Jacksons figure, but it was assumed that in the neighbourhood of 26 gms/100 ccs. the Landolt formula represented sufficiently closely the rate of change of specific rotation with concentration. Accordingly a specific rotation-concentration curve was drawn, parallel to Landolt's, but passing through 66.529 at 26.016 gms/100 ccs., and this used to determine the specific rotation at the various concentrations employed.

Solutions were made up and read at 20°.C, a 200 mm. water-jacketed tube being used in the polarimeter. All flasks were standardised initially and checked during the course of the work. The length of the polarimeter tube was measured with a large micrometer gauge and found to be 200.034 mms. at 20° .

REDUCING SUGARS. The potassium ferrocyanide modification of Main's method (23) is very suitable for the determination of small amounts of reducing sugars in the presence of large amounts of sucrose, and was used for the estimation of reducing sugar content of sugars and solutions. The full details of the method will not be given as these are available in the paper referred to above.

The method consists essentially in heating in a boiling water bath, three or more large test tubes containing increasing appropriate amounts of a solution of the sucrose, a fixed volume of extra-alkaline Fehling's Solution containing potassium ferrocyanide, and two drops of methylene blue solution, air being excluded during the heating by means of floats placed in the tubes: the proportions used are such that at the end of a definite time some of the tubes are still blue, while one at least (containing the greatest proportion of the sucrose solution) shows complete reduction (i.e. colourless solution). The Fehlings solution is standardised initially under identical conditions with solutions of known reducing sugar content. The method is suitable for the estimation of reducing sugar contents of sucrose solutions down to about 0.001%.

ASH. The standard sulphate ash method, as commonly used in sugar analysis was employed.

10 gms. of sucrose, or an amount of solution containing 10 gms., were treated with a little concentrated sulphuric acid in a platinum dish, heated with a bunsen until carbonised, and ignited at 500°C. to constant weight.

pH: The pH values of solutions were determined with a Morton type glass electrode and electrometer valve potentiometer. (The Cambridge Instrument Co. "pH Meter").

(c) Method of Expressing Supersaturation of Solution.

A number of alternative methods are possible for the expression of degree of supersaturation of a solution. That most commonly used in technical sugar work is the supersaturation coefficient of Claasen (24).

$$S_W = \frac{\text{Gms. sucrose per 100 gms. water in given solution at } T^{o}C}{\text{Gms. sucrose per 100 gms. water in saturated Solution at } T^{o}C}$$

The expression most commonly used in published work on velocity of crystallisation is based on the volume concentration of solution and is given as follows:

S_v = (Gms.solute per 100ccs.in given solution at T°C)—(Gms. solute per 100ccs.in Saturated Solution at T°C.)

The Fick diffusion equation introduces a volume concentration team, and since, starting with Noyes and Whitney, the interdependence of diffusion, and velocity of crystallisation has received much attention, the majority of investigators have expressed supersaturation by the second method. The volume concentration also enters into most equations employed in heterogoneous reaction kinetics.

In the tables given in the later sections of the Thesis, both supersaturation figures have been included, although the second expression, based on volume concentration, has been mainly used in the discussion of results.

In the analysis of solutions, sucrose concentrations are obtained as gms. per 100 gms. solution; these may be calculated directly to gms. per 100 gms. water, and the Claasen supersaturation figure found.

For the volume concentrations the very complete density tables (D^{20}_{4}) of the Kaiserliche Normal-Eichungs Kommission (25) for pure sucrose solutions have been used. The tables also include densities at temperatures ranging from 25°- 60°C and for concentrations up to 70 gms. per 100 gms. solution, and enable densities of supersaturated solutions at temperatures other than 20° to be found. In the cases of solutions of concentration higher than 70 gms/ 100 gms. solution, the figures for the required temperature were plotted against concentration and the curve entrapolated. Corrections found from this curve were applied to the densities at 20° to give the required density at the temperature of the experiment.

As the supersaturation is a difference term, a serious error is not introduced if densities at 20° C are taken for the calculation. A numerical example may be taken to illustrate this.

A solution at 40° C has a concentration of 73.00 gms. per 100 gms. solution. The solubility of sucrose at that temperature is 70.17 gms/100 gms. solution. Then,

1) Supersaturation Calculated from densities at 20°

	Conc. by Wt.	D^{20}_{4}	Conc. by volume
Given solution	73.00	1.36614	99.73 gms/100 ccs.
Satr. solution	70.17	1.34824	94.61 " " "
		Supersaturation =	5.12 " " "

2) Supersaturation calculated from densities at 40°

	Conc. by Wt.	D^{40}_{4}	Conc. by volume
Given solution	73.00	1.35505	98.92 gms/100 ccs.
Satr. solution	70.17	1.33730	93.84 " " "
		Supersaturation =	5.08 " " "

i.e. in this case the supersaturation calculated from densities at 20° is 0.7% high.

Although the differences are not large as can be seen from the above example, the more exact method of calculation at the actual temperature of the experiment has been used.

(d) Solubility of Sucrose.

The calculation of supersaturation by either method involves a knowledge of the solubility of sucrose at various temperatures. As there was some doubt as to the accuracy of the previously accepted figures of Herzfeld (26) a redetermination was made using a new method.

The details of the solubility work have for convenience been included as a separate section, Part 2, of the Thesis (pp. 112 — 125).

Results indicated that Herzfeld's figures were appreciably in error, particularly at high temperatures, and the writer's values have been used for the calculation of degree of supersaturation.

As shown in Part 2, the solubility of sucrose in pure solution at various temperatures may be expressed by means of the quadratic parabola.

$$C = 66.256 + 0.1497\, t + 0.000578\, t^2$$

Where C = concentration in gms/100 gms solution

and t = temperature °C.

A condensed table of solubilities at intervals of 5°C. is given on the following page.

TABLE 1.

Solubility of Sucrose

Temperature °C.	Solubility (gms/100 gms.solution)
20	66.48
25	67.36
30	68.27
35	69.20
40	70.17
45	71.16
50	72.19
55	73.24
60	74.32
65	75.43
70	76.57
75	77.74
80	78.93

(4) Crystals.

(a) Growth and Selection of Initial Crystals. The accuracy of the measurement of crystallisation velocity, particularly as regards growth rates of individual crystal faces, depends very largely on the degree of perfection of the crystals used for the work. Sucrose crystals in general show a marked tendency towards irregularity, and some difficulty was experienced in obtaining satisfactory crystals for the experiments.

Preliminary work showed that crystals measuring about 5 mms. along the b axis and weighing about 0.05 gms. were a convenient size to use, and could be measured and weighed with sufficient accuracy. The growth of crystals much larger than this requires considerably more time, and would not add to the accuracy of the work.

Crystals used in the earlier experiments were grown from very slightly supersaturated solution, contained in a wide-mouthed bottle arranged so that it could be rotated with axis horizontal in a thermostat. When growing crystals from solution in this manner, high supersaturations cannot be employed since spontaneous crystallisation takes place rapidly throughout the bulk of solution, fine crystals adhere to the faces of the larger ones, and deformation results.

Crystals were grown at 25°C, the pure solution being made up so as to be saturated at about 30°C. This low degree of supersaturation makes the process of growth a very slow one, and when starting from microscopic crystals may extend to several weeks. The solution is changed two or three times during the course of the growth.

For the removal of the viscous solution adhering to the crystals, alcohol saturated with sucrose at room temperature was used. After removing from solution the crystal was pressed between filter papers to remove the greater part of adhering solution, held under a fine jet of the alcohol, and the various faces wiped carefully with a piece of chamois leather. The method was found to be very satisfactory, and as will be shown later (p 64) enables reproducible weights to be obtained.

As only a small proportion of the crystals grown in this manner were sufficiently perfect for use in the velocity of crystallisation experiments, and as the process was extremely slow, the possibility of using commercial crystals of sucrose was investigated. The commercial grade of refined sugar termed "coffee sugar" contains crystals of approximately the required size, although the industrial method of separating crystals from solution and the consequent treatment they receive results in the greater proportion of them being eroded or partly broken. Through the courtesy of Messrs. Tate and Lyle Ltd., samples of solution containing crystal were obtained during the progress of crystallisation under vacuum. After removing and cleaning these crystals with alcohol, it was found that a fair proportion of them were sufficiently perfect and only required a little extra growth to bring them up to about 5 mm. size. Crystals obtained in this manner were used for the greater part of the work.

All crystals were examined under a travelling microscope for parallelism of edges and faces, and freedom from any other irregularities, and only those satisfactory in all respects were used for the velocity of crystallisation experiments.

(b) Measurement of Growth of Individual Crystal Faces.

The accurate measurement of the growth of individual faces of a crystal ~~and~~ in a normal direction presents a number of difficulties and no altogether satisfactory method for this appears to have been reported in the literature.

The method used by Bentivoglio (18) did not seem to lend itself to the present work since it involved the rigid attachment of the crystal to a holder, and permitted the measurement of only a limited number of faces. Amongst other methods which have been used is that of measuring the distance between two opposite and parallel faces of the crystal before and after growth by means of a micrometer. With this method it has to be assumed that the two faces grow at equal rates, and furthermore the convenient measurement with a micrometer is not always possible unless the faces are sufficiently large. In the case of small crystals of sucrose the distance between the $\{100\}$ faces is practically the only one which can be measured in this manner.

The method finally developed involves the linear measurement of the various faces of the crystal under a travelling microscope, a number of faces being marked with black reference spots to enable growths of the faces in the normal direction to be calculated.

Before proceeding with the description of the method, however, it is necessary to deal first with the crystallography of sucrose as a knowledge of this is required.

CRYSTALLOGRAPHY OF SUCROSE. A clinographic projection of the crystal as usually obtained from pure solution is given in Figure 6. Sucrose belongs to the monoclinic system sphenoidal class, the b axis being the two-fold axis of symmetry, and the polar axis of the crystal. The a and c axes are inclined to one another, while the b axis is perpendicular to both. Axes are of unequal lengths.

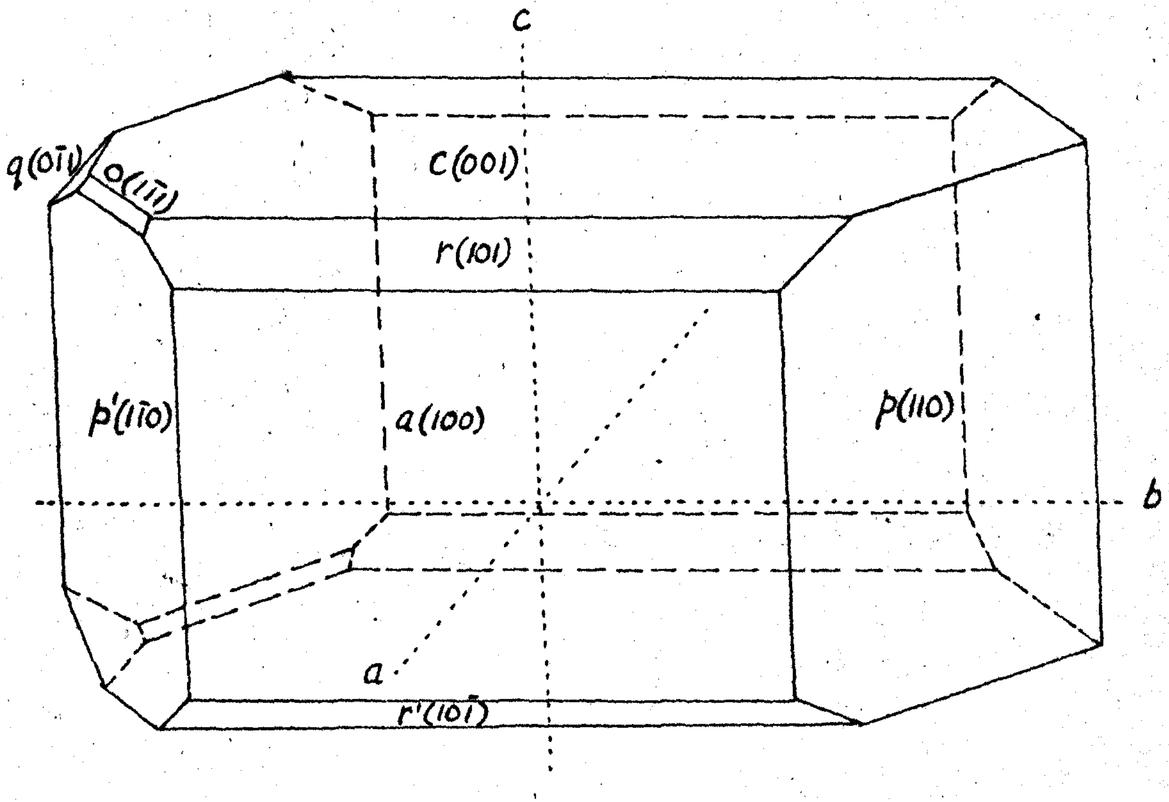
The following forms generally occur:

a $\{100\}$, c $\{001\}$, r $\{101\}$, r^1 $\{10\bar{1}\}$, p $\{110\}$,
p^1 $\{1\bar{1}0\}$, q, $\{0\bar{1}1\}$, and o $\{1\bar{1}1\}$.

In the crystals obtained by the writer, and used for the velocity of crystallisation measurements, the clinodomes and hemipyramid faces, $\{0\bar{1}1\}$ and $\{1\bar{1}1\}$ respectively were generally very small or absent. Less frequently occurring forms were the $\{210\}$ and the clinodomes at the other pole of the crystal, $\{011\}$.

A number of other forms have been reported, including the $\{410\}$, $\{530\}$ and $\{320\}$ but these have never been found on any of the crystals obtained by the writer from pure solution.

The various interfacial angles reported by different workers show differences amounting in some cases to about 2°, doubtless due to the difficulty of obtaining crystallographically perfect crystals. It is doubtful if the high



— FIGURE 6. —

degree of accuracy commonly obtained with most inorganic crystals will ever be attained with sucrose, even after the most careful growth and selection of crystals.

Redetermination of the more important angular values were made during the progress of the work. The analytical samples of solutions taken in the various experiments all crystallised out on standing and a selection of the best crystals was made for the goniometric investigation. Crystals were carefully cleaned with alcohol saturated with sucrose and kept in a desiccator.

The Fuess horizontal circle goniometer which was used for the work has been fully described by Tufton (27) Vol.I pp.33-42, and need not be dealt with here. Standard technique was employed, both as regards preliminary adjustment of the goniometer and the determination of the angular values.

Some forty of the best crystals were first examined with the goniometer, and from these, thirteen selected which gave good single reflections from a number of faces. The angles given in the second last column of Table 2 are the means of the reliable determinations, values found from faces giving double or blurred reflections being neglected.

TABLE 2.

Interfacial Angles of Sucrose

Face	Face Symbols	Hankel (1840)	Miller (1842)	Wolff (1843)		Rammelsberg. (1855)	Schaaf (1881)	Rinne (1885)	Vavrinecz. (1925)	Phelps (1931)	Vernon	Value Taken
				Meas.	Calc.							
a:c	100:001	76°30'	75°30'	76°30'	-	76°43'	76°44'	76°15'	77°5'	76°25'	77°3'	77°4'
a:r	100:101	-	-	-	46°15'	45°37'	-	-	45°11'	44°31'	-	45°11'
a:r'	$100:10\bar{1}$	63°45'	63°20'	-	64°30'	64°27'	64°12'	63°12'	63°14'	63°32'	63°17'	63°19'
c:r	001:101	-	-	-	30°15'	31°20'	-	-	31°50'	31°42'	-	31°50'
c:r'	$001:\bar{1}01$	39°45'	41°10'	39°0'	-	39°17'	39°4'	-	39°45'	40°0'	39°42'	39°49'
c:q	$001:0\bar{1}1$	-	-	-	40°30'	-	-	-	41°5'	40°19'	40°58'	41°1'
q:q	$011:0\bar{1}1$	-	-	-	99°0'	-	-	-	-	98°0'	98°4'	98°2'
r:o	101:111	-	-	-	32°24'	-	-	-	-	32°52'	-	32°52'
a:p	100:110	50°0'	-	-	50°48'	50°46'	-	50°40'	50°37'	50°44'	50°31'	50°41'
p:p	$110:\bar{1}10$	80°0'	79°20'	78°28'	-	78°30'	78°30'	78°48'	78°41'	78°43'	78°52'	78°43'
p_2:a	210:100	-	-	-	-	-	-	-	31°11'	-	-	31°11'
p_2:p	210:110	-	-	-	-	-	-	-	19°26'	-	-	19°26'

Published data on Sucrose goes back to 1840. Groth (28) Vol.3 p.448 quotes four series of values by Wolff (29), Rammelsberg (30) Miller (31) and Hankel (32) and accepts Wolff's figures for the calculation of the axial ratios. In addition to the above results there are also those of Rinne (33), and the more recent determinations of Phelps (34) and Vavrinecz (35). The last column of the Table shows the angular values which have been taken for the purposes of the work on velocity of crystallisation. They have been arrived at by selecting and averaging what were thought to be the more reliable determinations, more weight being given to those values based on a large number of determinations.

It may be added that the axial ratios given in Groth (28), based on Wolff's data are :

$$a : b : c = 1.2595 : 1 : 0.8782 \ . \quad \beta = 103^{o}30^{1} \ .$$

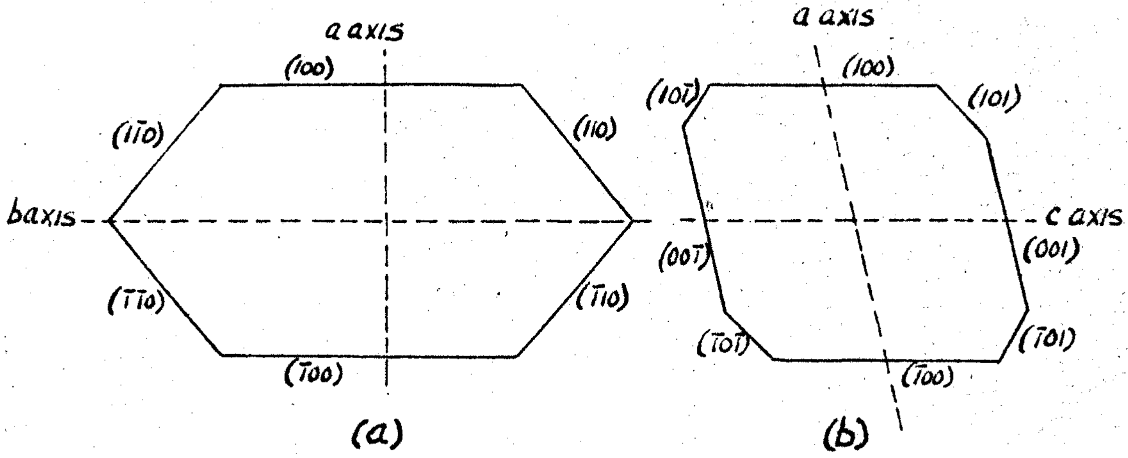
Vavrinecz gives a value for the axial angle of $\beta = 102^{o}55^{1}$, this being based on the mean of 150 readings. The mean value found by the writer was $\beta = 102^{o}57^{1}$ which is in good agreement with Vavrinecz. Axial ratios calculated by Vavrinecz are

$$a : b : c = 1.2518 : 1 : 0.8946 \ . \quad \beta = 102^{o}55^{1}.$$

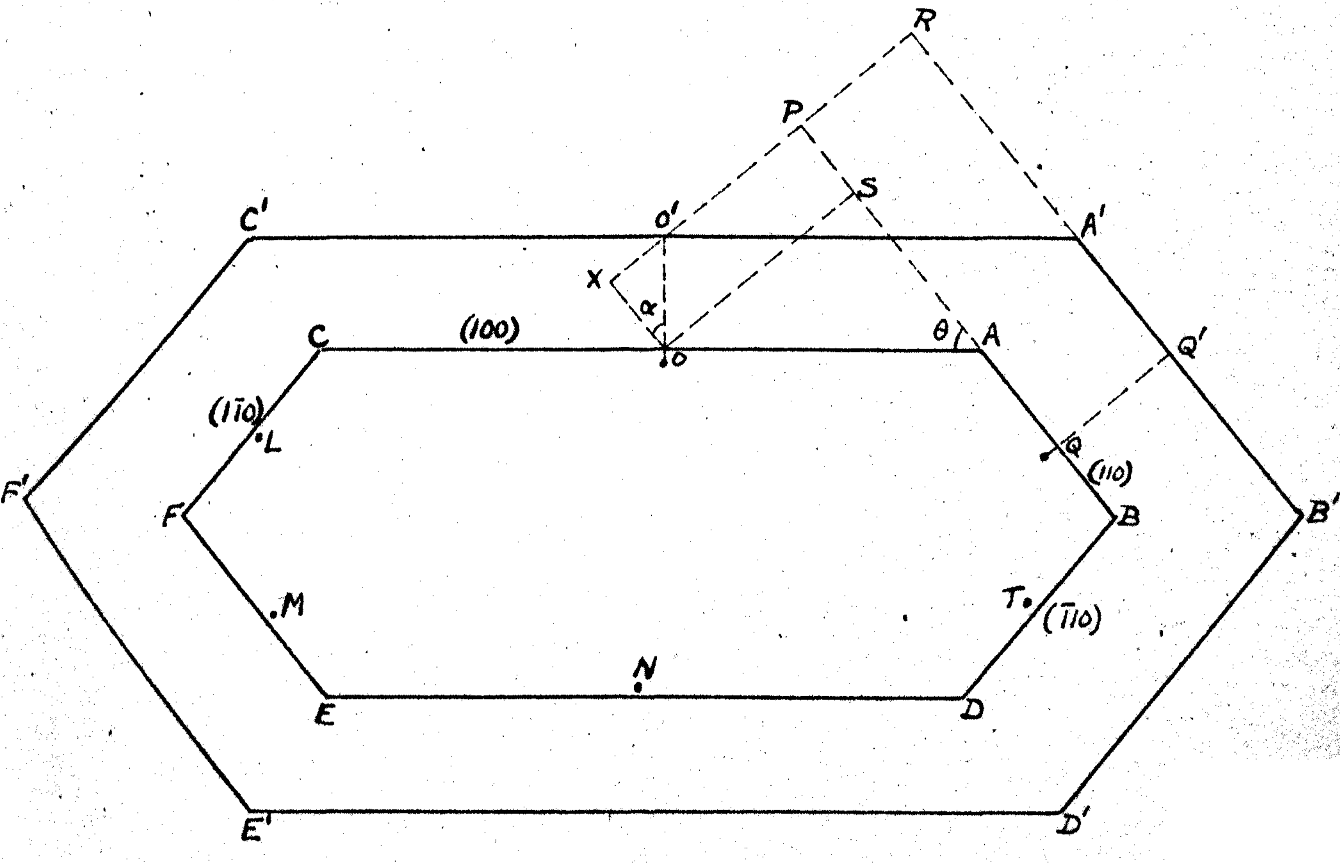
MEASUREMENT OF GROWTH. The two most important zones of the crystal are the [010] zone, parallel to the c axis, and the [001] zone, parallel to the b axis. These two zones, which are shown in Figure 7 together include 12 faces of the crystal. The two left clinodomes $\{0\bar{1}1\}$, which frequently occur lie in the [100] zone, which includes the $\{001\}$ faces, while the hemipyramids $\{\bar{1}11\}$ are in the [101] zone with the $\{101\}$ faces.

Before using a crystal for an experiment, reference spots were made on a number of faces. A very small mark was made with the point of a needle in the centre of a face, and this blackened, with a hard pencil which had been ground to a very fine point. After marking the requisite number of faces in this manner the crystal was allowed to grow for a couple of hours in slightly supersaturated solution in a thermostat, and finally removed and cleaned with alcohol as described previously. Provided that the marks on the faces are only very small, the crystal will grow evenly over the spots. Four pairs of faces were marked in this manner: the $\{100\}$, $\{110\}$, $\{1\bar{1}0\}$ and $\{001\}$ forms.

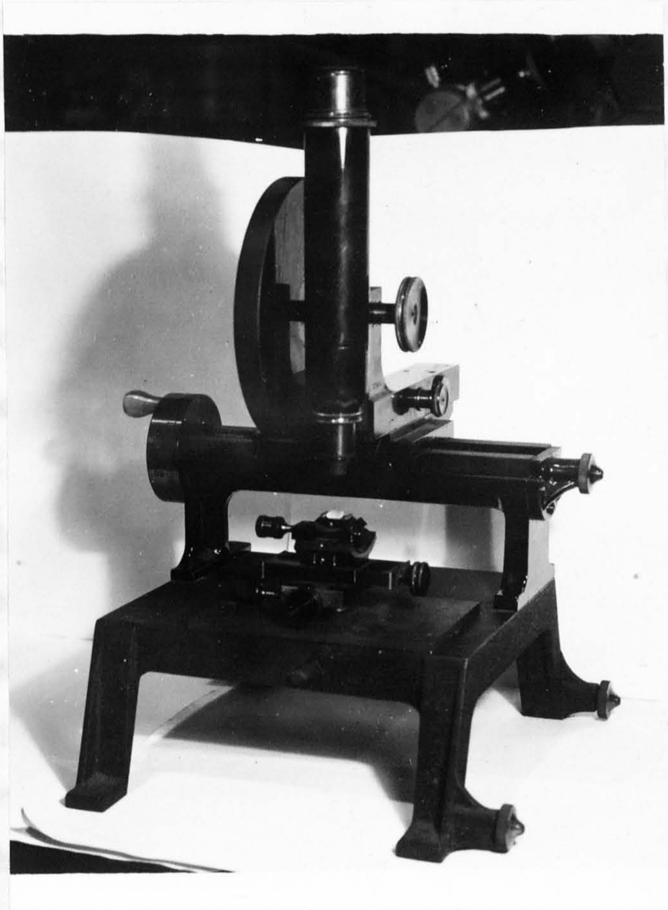
For the measurement of the crystals, the crystal adjusting movement of the Fuess goniometer was attached to a flat brass plate and the latter placed on the platform



— FIGURE 7 —



— FIGURE 9 —



— FIGURE 8. —

of a Beck travelling microscope as shown in the photograph Figure 8. Removing the centre peg normally used with the goniometer, a crystal could be placed on top of the movement and tilted in any direction by means of the two mutually perpendicular tangent screws.

Commencing with the measurement in the [010] zone, the case of the (100) and (110) faces will be dealt with in detail to illustrate the method. In Figure 9 ABDEFC represents the crystal before growth, while $A^1B^1D^1E^1F^1C^1$ is the same crystal after growth. Reference spots are at O, Q, T, N, M, and L.

Before the growth experiment, the crystal is placed on the goniometer stage and adjusted by means of the tangent screws until the (100) face is at right angles to the axis of the microscope; i.e., until all parts of the face are in sharp focus when traversed with the microscope. The cross hair in the eyepiece is adjusted so as to be perpendicular to the direction of travel of the microscope, and the flat plate carrying the goniometer movement with crystal moved slightly if necessary to bring the edges A and C of the crystal parallel to the cross hair. Having made these adjustments the perpendicular distances O A and O C from the edges to the spot are measured. The spot in general is irregular and of much larger diameter than the cross hair, but this does not interfere with the accuracy of the reading as the distances are measured from one side of the spot. By adopting a convention as regards the placing of the crystal, and by always traversing from left to right, no confusion arises as to which edge to take.

The preliminary levelling of a face was carried out with a magnification of about x 80, while the actual measurement was more conveniently done with a lower magnification of about x30

The crystal is now tilted so that the (110) face is perpendicular to the axis of the microscope and the distances QA and QB found, taking the precautions mentioned above.

After growth the crystal is again placed in position under the microscope and the new (100) face A^1C^1 adjusted so as to be perpendicular to the axis. The spot o can still be seen clearly underneath the layer of crystal, and the distances O^1A^1 and O^1C^1 may be found. Similarly Q^1A^1 and Q^1B^1 are measured on the new (110) face.

When taking a reading for a spot, the microscope has, of course, to be focused down as the spot is below the level of the surface. Since the axis of the microscope is always adjusted perpendicular to the face, no refraction error is introduced when measuring from a spot some distance below the surface.

To calculate the growths of the (100) and (110) faces, only O A, Q A, and their corresponding distances after growth, O^1A^1 and Q^1A^1 are required. The other distances O C, Q B, etc. are used for calculations of other faces. For the case of the (100) and (110) faces the construction shown in Figure 9 may be taken.

From the spot at O, draw OO^1 perpendicular to CA, cutting the faces CA and C^1A^1 at O and O^1 respectively. Similarly draw QQ^1 perpendicularly to AB. Produce BA and B^1A^1 to P and R respectively and from O and O^1 draw OS and O^1R perpendicular to AP and AR. From O draw OX perpendicular to PO^1 produced to X.

$$\text{Then: } AS = OA \cos\theta$$

$$\text{and } A^1R = O^1A^1 \cos\theta$$

$$QS = QA + OA \cos\theta$$

$$\text{and } QR = Q^1A^1 + O^1A^1 \cos\theta .$$

$$\text{Hence } OO^1 = \frac{OX}{\cos\alpha} = \frac{Q^1R - QS}{\cos\alpha}$$

$$= \frac{Q^1A^1 - QA + \cos\theta\,(O^1A^1 - OA)}{\cos\alpha}$$

θ is the interfacial angle, which for these faces is $50^{\circ}41^{1}$ from Table 2 and α is the complement, $39^{\circ}19^{1}$.

$$\therefore OO^1 = \frac{(Q^1A^1 - QA) + \operatorname{Cos} 50^{\circ}41^{1}\,(O^1A^1 - OA)}{\operatorname{Cos} 39^{\circ}19^{1}}$$

$$= 1.2927(Q^1A^1 - QA) + 0.8190(O^1A^1 - OA) .$$

Further,

$$OS = OA \quad \sin\theta$$

And $O^1R = O^1A^1 \sin\theta$.

and also in the $\Delta\, OXO^1$

$$XO^1 = OO^1 \quad \sin\alpha.$$

Hence:

$$QQ^1 = XR - OS$$

$$= O^1A^1 \sin\theta + OO^1 \sin\alpha - OA \sin\theta .$$

$$= (O^1A^1 - OA) \sin\theta + OO^1 \sin\alpha$$

$$= 0.7736(O^1A^1 - OA) + 0.6336\ OO^1$$

The formulae for the (100) and (110) faces are therefore:

$$\left.\begin{aligned} OO^1 &= 1.2927\ (Q^1A^1 - QA) + 0.8190\ (O^1A^1 - OA\ ) \\ QQ^1 &= 0.7736\ (O^1A^1 - OA) + 0.6336\ \ OO^1 \ . \end{aligned}\right) - (1)$$

The same formulae may be applied to measurements of the faces adjoining the edges C, E and D, and thus by measuring round the zone of faces shown in Figure 9 the

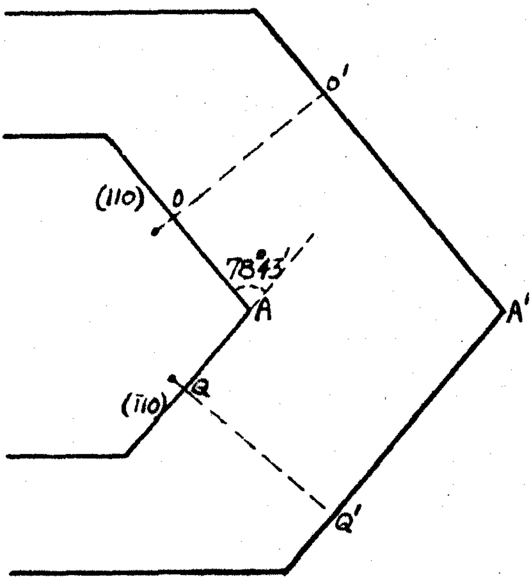
the vertical growths of the six faces of the zone may be found. The growths of the (100) and (100) faces are checked from measurements at both the left and right ends of the crystal.

Independent calculation of the growths of the $\{110\}$ and $\{1\bar{1}0\}$ faces is possible if measurements from their common edges are taken. Figure 10 shows the (110) and $(\bar{1}10)$ faces, with the lettering O, A, Q, etc. given to conform with the previous case. The interfacial angle is $78^{\circ}43^{1}$ and the equations become :

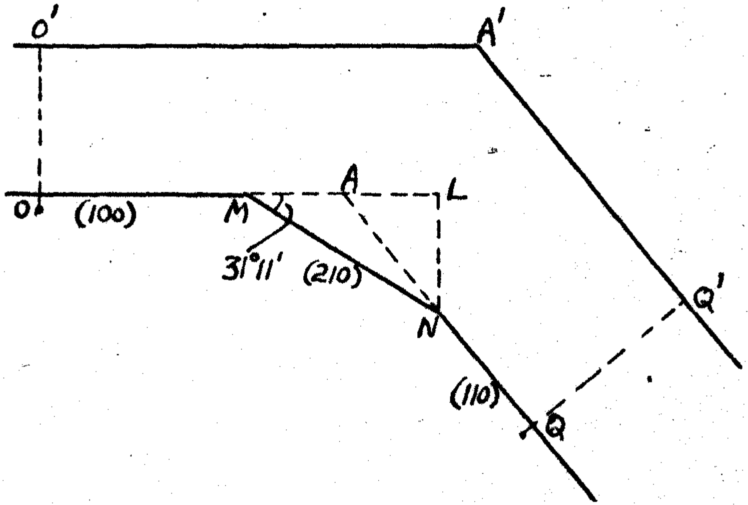
$$\left.\begin{aligned} OO^{1} &= 1.0197\,(Q^{1}A^{1} - QA) + 0.1994\,(O^{1}A^{1} - OA) \\ QQ^{1} &= 0.9807\,(O^{1}A^{1} - OA) + 0.1456\ \ OO^{1} \quad . \end{aligned}\right\} \text{— (2)}$$

Occasionally a small (210) face was observed in the original crystal, although this had always disappeared on the crystal after growth. The presence of this face may be corrected for as follows:

Fig.11 shows the crystal before and after growth, the (210) face being present in the original crystal and absent in the final one. When measuring the (100) face, the distance OM is found, and also the (210) face measured in projection; i.e., ML is determined.



— FIGURE 10 —



— FIGURE 11 —

If OM and QN are produced as in Fig.11 their point of intersection A will represent the hypothetical position of the (100) : (110) edge. From a knowledge of the interfacial angles (see Table 2), MA and NA can be calculated and added to OM and QN to give OA and QA respectively.

The calculated values are :

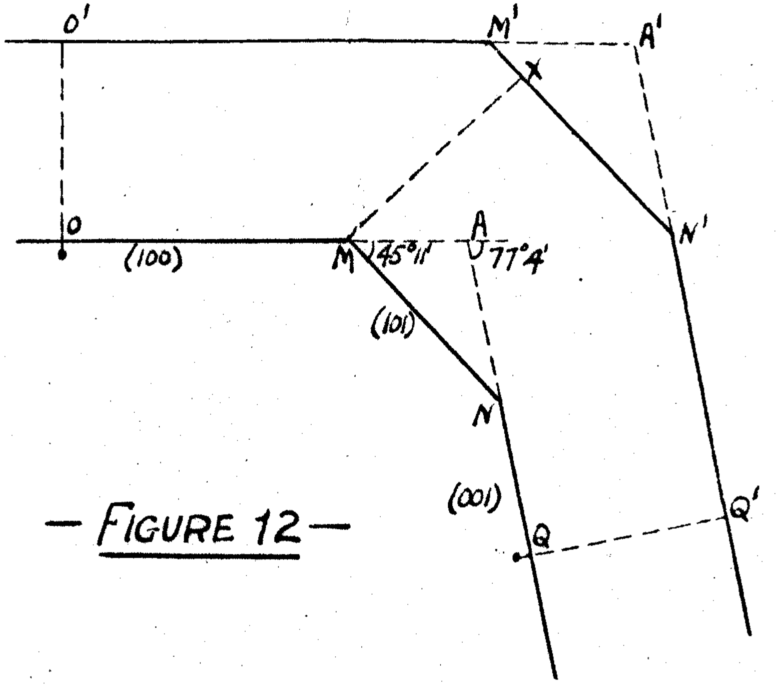
$$\left.\begin{aligned} MA &= 0.503\ ML \\ NA &= 0.783\ ML \end{aligned}\right\} - (3)$$

Having applied these corrections for the presence of the (210) face, formulae (1) may be used as before to give OO^1 and QQ^1.

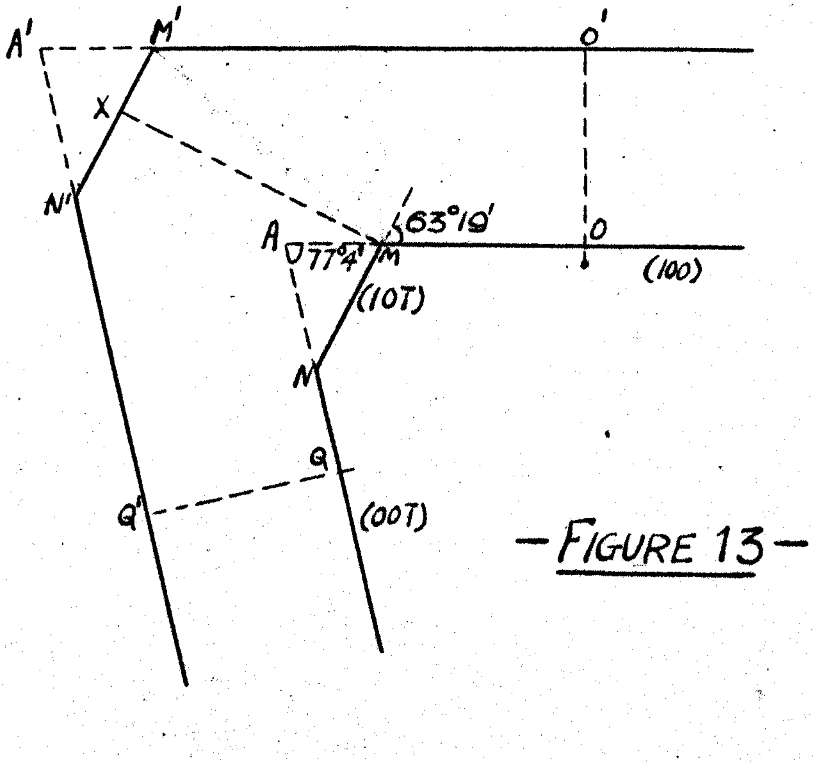
The measurement in the [001] zone of faces, parallel to the b axis (see Fig. 7 b.) is similar in principle. Since in the crystals used for the work the $\{101\}$ and $\{10\bar{1}\}$ forms were too small to mark, only four of the eight faces of the zone had reference spots.

Taking first the (100), (101) and (001) faces (see Figure 12), OM, O^1M^1, and QN, Q^1N^1 are measured as before, the crystal adjusted so that the (101) face ~~was~~ is perpendicular and the breadth of this face, MN and M^1N^1 found.

As in the case of the (210) face dealt with above, the positions of the hypothetical edges A and A^1 can be calculated, since:



— FIGURE 12 —



— FIGURE 13 —

$$\left.\begin{aligned} AM &= 0.5413\ MN \\ \text{and}\quad AN &= 0.7279\ MN \end{aligned}\right) \quad - \quad (4)$$

and similarly for M^1N^1.

Having added these amounts to OM, QN, etc., OO^1 and QQ^1 are given by :

$$\left.\begin{aligned} OO^1 &= 1.026\ (Q^1A^1 - QA) + 0.2297\ (O^1A^1 - OA) \\ QQ^1 &= 0.9747(O^1A^1 - OA) + 0.2238\ \ OO^1 \end{aligned}\right) \quad - \quad (5)$$

As regards the perpendicular growth of the unmarked (101) face, it can be shown that the growth of this face is given by :

$$MX = 0.7094\ (O^1M^1 - OM) + 0.7048\ OO^1 \quad - \quad (6)$$

For the (100), $(10\bar{1})$ and $(00\bar{1})$ faces shown in Figure 13, a similar reasoning to the above can be applied.

The distances AM, AN, etc. are given by

$$\left.\begin{aligned} AM &= 0.6541\ \ MN \\ AN &= 0.9167\ \ MN \end{aligned}\right) \quad - \quad (7)$$

and similarly for A^1M^1 and A^1N^1 .

After adding these to the measured distances OM, QN, etc., OO^1 and QQ^1 are given by

$$\left.\begin{aligned} OO^1 &= 1.026(Q^1A^1 - QA) \ - \ 0.2296\ (O^1A^1 - OA) \\ QQ^1 &= 0.9747(O^1A^1 - OA) - \ 0.2238\ \ OO^1 \end{aligned}\right) \quad - (8)$$

The growth of the $(10\bar{1})$ face may be found by a formula analagous to that for the (101) face, the growth of this face, MX, being given by :

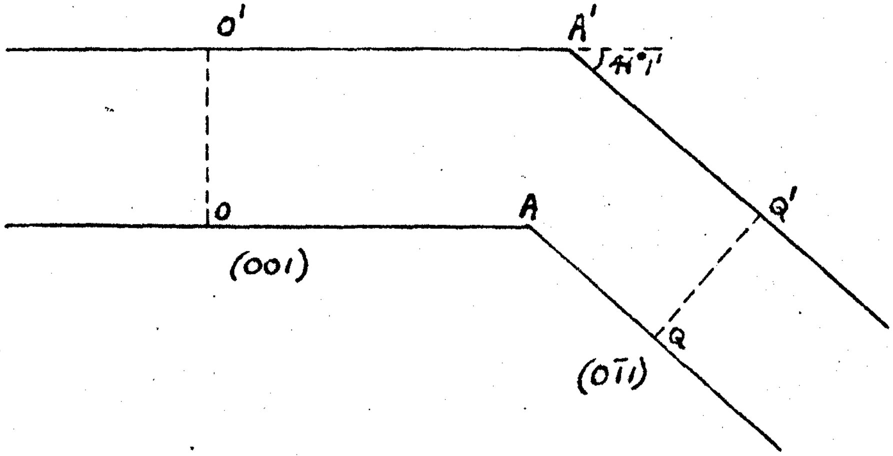
$$MX = 0.8935\ (O^1M^1 - OM) + 0.4491\ OO^1 \quad — \quad (9)$$

The <u>clinodomes</u> q $\{0\bar{1}1\}$ do not occur in either of the two zones dealt with above, but belong to the [100] zone which includes the {001} faces. Figure 14 shows the two faces in question before and after growth, the interfacial angle (from Table 2) being $41^{o}1^{1}$.

The clinodomes on the crystals obtained were too small to mark but since OO^1 the growth of the (001) face may be found independently from measurements in the [001] zone, calculation of the growth of the $(0\bar{1}1)$ face follows directly if the distances OA and O^1A^1 are measured. The normal growth of the clinodome is:

$$QQ^1 = 0.6563\ (O^1A^1 - OA) + 0.7546\ OO^1 \quad — \quad (10)$$

If the right clinodomes {011} are present at the other end of the crystal, the same formula may be applied to calculate their growth.



— FIGURE 14.—

The only faces of the crystal shown in Figure 6 which have not been considered are the two hemipyramids, $o\{1\bar{1}1\}$. These were always so small that measurement of them was not attempted.

Thus by marking the crystal, measuring before and after growth, and applying equations (1)-(10) as described in the above section, the normal growths of fourteen faces may be found. The $a\{100\}$ faces are measured at the four edges, common to the $p\{110\}$, $p^1\{1\bar{1}0\}$, $r\{101\}$, and $r^1\{10\bar{1}\}$ forms. Two independent values are obtained for the $c\{001\}$ faces by measurements relative to the $r\{101\}$ and $r^1\{10\bar{1}\}$ edges, while the prism faces $p\{110\}$ and $p^1\{1\bar{1}0\}$ are checked by reference to the $a\{100\}$ edges, and to the end prism edges.

(c) Determination of Weight of Sucrose Crystallised.

Kucharenko's method for the determination and expression of crystallisation velocity has been described on pp 3—6 . For the purposes of comparison with his results, the increase in weight of crystals was determined in addition to the measurement of the growth of individual faces as described in the last section.

It will be recalled that Kucharenko's method involves a knowledge of the weight/surface area relationships of crystals, and to check the method redeterminations were made. A knowledge of the density of the crystals is also necessary.

The weights of crystals were determined after cleaning with alcohol and drying at 35°C. over CaO, under a vacuum of about 0.01 mms. It was found that constant weight was reached after about 3 hours. Crystals were weighed in small stoppered weighing bottles with an accuracy of 0.1 mgms.

For the measurement of surface areas, a Hutchinson coordinate micrometer scale, ruled with lines 0.1 mm. apart was inserted in the occular of the travelling microscope. Using the goniometer stage, each face of a crystal was adjusted so as to be perpendicular to the axis, and the magnification chosen so that the face was entirely in the field of view of the microscope. With correct adjustment of the lighting, the face could be seen clearly against the ruled grating and the area found by counting the number of squares covered.

The area corresponding to one square of the grating was found by making use of the measuring arrangement of the travelling microscope. With the magnification most generally employed, one square corresponded to an area of 1.499×10^{-5} cm^2.

The method is tedious, but enables surface areas of small crystals to be estimated to within about ±0.6% as will be shown later. In a few cases, photographs were taken and the squares counted from the negatives, but the extra work entailed in the photography makes the direct visual counting preferable.

The densities of small crystals may be most accurately determined by means of a flotation method.

Convenient liquids for sucrose are carbon tetrachloride and toluene. As the former has a density of 1.5947 at 20°, compared with the value for sucrose of about 1.58, only a small amount of toluene (D_4^{20} = 0.8660) is required to make the mixture.

25 cc. measuring cylinders with ground stoppers were filled with carbon tetrachloride and suspended in a thermostat at 20°.00 ± 0°.02 C. After adding a dried sucrose crystal, toluene was added drop by drop, shaking the cylinder after each addition, until the point was reached when the crystal remained practically stationary in the solution.

The density of the solution, which was then equal to the density of the crystal, was determined by pycnometer in the usual manner.

(5) Method of Carrying out an Experiment.

Having described in the preceeding sections 2, 3 and 4, the apparatus and individual stages of the experimental technique, the method of carrying out a velocity of crystallisation experiment will be described.

The required number of selected and marked crystals were first measured with the travelling microscope as described on pp. 41 to 50 . To ensure that the crystals were perfectly clean, they were washed a second time with alcohol, pressed between clean filter papers, transferred to the weighing bottles, and after drying to constant weight in vacuum, their respective weights found. After the second washing with alcohol, the crystals were handled with rubber-tipped forceps and not touched by hand.

Having cleaned the crystallisation apparatus and allowed excess water to drain from the coils, flat glass plates were fitted to the cells, and the supersaturated solution prepared as described previously added gradually to the reservoir and pumped round the circuit. About the first 200 ccs. flowing from the final thermostat coil were discarded, as the traces of water still remaining in the coils caused a slight dilution. After circulation had commenced solution was added to the reservoir until it contained about 700 ccs. and the thermocouples inserted.

The approximate concentration of the solution was known from a refractometer determination, and the temperature at which the solution would be saturated was found from the solubility table. The heating bath was adjusted until the ~~ex~~exit temperature of the solution was about 5° above the calculated saturation temperature, and the other thermostats adjusted to the required experimental temperature. After steady temperature conditions had been reached, (generally within about 30 minutes), the crystals were transferred to their respective holders, the glass cover plates removed from the cells, and the crystals inserted and centered, the time being noted in each case.

The rate of flow of solution in the circuit was then determined by swinging the inlet tube away from the reservoir and collecting about 200 ccs. of solution in a tared bottle, the time of delivery being taken with a stop watch. The rate of flow in ccs. per second could be calculated.

The solution obtained was analysed as described on pp 24–27 . After taking the sample a rubber sleeve was finally fitted over the inlet to the reservoir.

The temperature of solution entering the cells was recorded at 5 minute intervals in the shorter experiments lasting about 2 hours, and at 15 minute intervals when investigating low supersaturations, where it was necessary to extend the time up to about 8 hours.

At the conclusion of the experiment the rate of flow was again determined, giving a second sample for analysis, the crystals withdrawn from the cells and solution quickly removed with alcohol, the time of withdrawal being noted in each case.

The crystals were dried to constant weight, and finally measured with the travelling microscope. In a number of cases surface areas and densities were also determined before and after growth.

III ACCURACY OF THE EXPERIMENTAL METHOD.

Estimates of the probable accuracy of the various determinations involved in the experimental method are given below.

(1) Supersaturation of Solutions.

The concentration of sucrose in a given solution, determined polarimetrically as described previously, may be estimated with an accuracy of ± 0.02 gms/100 gms. solution. Duplicate and sometimes triplicate determinations which were made for each solution investigated, agreed in all cases to within 0.04. The mean value should, therefore, have the accuracy given above. In the calculation to gms. per 100 ccs, the density figures are known with such accuracy that it can be taken that virtually no additional error is involved. The accuracy of the volume concentrations may therefore be put at about ± 0.03 gms. per 100 ccs. solution.

As mentioned previously, solutions were analysed initially, and at the completion of each experiment in order to verify that no concentration change through evaporation had taken place. In every case the initial and final determinations agreed to within experimental error, the average of all determinations showing a decrease of 0.01 gms/100 ccs. solution. It may be taken, therefore, that the concentration of solution during an experiment remains unchanged.

As the presence of reducing sugars in the solutions would cause errors in the polarimetric determinations due to their negative specific rotation, solutions were analysed initially and finally for reducing sugar content by the method described previously. The average reducing sugar contents for all experiments are as follows:

Initial solutions	0.007	gms/100 gms. solution
Final solutions	0.018	" " " "

If the reducing sugars are assumed to be composed of equal amounts of glucose and fructose, the specific rotation $[\alpha]^{20}_{D} = -20$. Calculation will show that the presence of reducing sugars in these amounts will have an inappreciable effect on the determination of sucrose.

The accuracy of the solubility figures for sucrose is discussed in Part 2 of the thesis. As will be shown later the solubility should be within ± 0.04 gms. per 100 gms. solution.

The supersaturation, (C - Co) of a given solution should thus be known to within ± 0.06 gms/100 ccs. solution.

Temperatures throughout the experiments were constant to at least ± 0.1° C, the effect of temperature errors being thus negligible.

(2) Growth Rates of faces.

The accuracy of the measurement of growth of individual crystal faces was checked in two ways:

(a) By carrying out duplicate determinations using double cells of the type shown in figure

(b) By comparing the growth of a face calculated with reference to different faces of the same crystal. It was shown previously that four separate estimations of the growth of the $\{100\}$ faces could be made, two of the $\{001\}$, and two of the $\{110\}$ and $\{1\bar{1}0\}$ faces.

In general experiments were continued until the faces of a crystal had grown about 0.2 - 0.6 mms., although at the lower temperatures of 25 and 30°, growths of less than this amount had to be measured on account of the slow rate of crystallisation.

It was found that the reproducibility obtainable varied somewhat from face to face. An analysis of the results of many experiments showed that the a $\{100\}$ and p $\{110\}$ faces gave the highest reproducibility. The measurement of the $p^1\{1\bar{1}0\}$, c $\{001\}$ and $r^1\{10\bar{1}\}$ faces was somewhat less accurate while for some reason which is not clear, the r $\{101\}$ faces showed a marked tendency towards irregularity of growth. Accurate measurement of the growths of the clinodome $\{0\bar{1}1\}$ faces also proved difficult. The growth measurements of these latter faces is dependent on the c $\{001\}$ faces and accordingly the accuracy would not be expected to be as high as in the other cases.

The following estimate of the accuracy of the measurement of growth rates of faces has been based on all the experiments carried out during the course of the work. It was found that errors of ± 5% are to be expected in the measurement of the growth rates of the a $\{100\}$ and p $\{110\}$ faces. With the p^1 $\{1\bar{1}0\}$, C $\{001\}$ and $r^1\{10\bar{1}\}$ faces the error is about ± 7%, while the r $\{101\}$ cannot be estimated closer than ± 10%.

The clinodome q $\{0\bar{1}1\}$ faces could only be measured in relatively few cases since if present on the crystal they were extremely small. The results obtained for these latter faces were so variable that they have been omitted from the tables given in Sections IV and V of the Thesis.

It was found that within the above limits of accuracy, the same growth rates were obtained whether the crystal was placed with right or left pole facing the stream of solution in a cell.

(3) Kucharenko's Method.

As it seemed desirable to compare results with those of Kucharenko, an examination of the accuracy of his method was made. As mentioned previously (p. 4) the assumption was made that the surface areas of similar crystals were proportional to the 2/3 power of the weights, i.e.,

$$S = K W^{2/3}$$

K was evaluated by measurements of very large crystals. A value of 4.12 ± 0.05 was found when surface areas were expressed in cm^2 and the weight in gms.

To check this constant, surface areas of 9 small crystals were measured using the method described on p. 51 .

In measuring the area of a face of a crystal by counting the number of squares covered in a coordinate eyepiece scale, the error introduced will be chiefly due to the uncertainty of estimating fractions of squares at the edges of the face. The possible error due to this cause however, is small, and duplicate surface area determinations carried out on several of the crystals agreed to within ± 0.6%.

The crystals could be weighed to within 0.1 mg. or about 0.2 - 0.3%.

Table 3 shows the surface areas of the various faces of the 9 crystals measured. Their corresponding weights and the values of K are given at the bottom of the table. The mean value found was 4.55 ± 0.12, 8% higher than Kucharenko's figure.

The accuracy of about 1% ascribed by Kucharenko to the value of K seems doubtful, and would hardly be expected in view of the fact that crystals generally show considerable differences in the relative development of faces. The areas of individual faces given in Table 3 illustrate this.
As the density of sucrose is involved in the constant K, density determinations of a number of crystals were made. The mean value obtained for 8 crystals was 1.5830 compared with 1.5850 as determined by Kucharenko. Errors due to density variations are therefore negligibly small.

TABLE 3.

Surface Areas of Sucrose Crystals

Face.		Surface Areas (sq. mms).				
		1	2	3	4	5
a	100	11.360	6.956	9.819	9.525	10.418
	$\bar{1}00$	11.229	10.528	9,769	9.742	11.206
p	110	3,590	4,626	2.508	3.538	6.456
	$\bar{1}10$	4.351	4.683	3.000	3.337	4.603
p^1	$1\bar{1}0$	3.423	2.937	2.538	3.252	5.066
	$\bar{1}\bar{1}0$	3.805	5.947	2.510	3.336	6.026
c	001	6.410	6.863	6.107	5.449	7.200
	$00\bar{1}$	4.876	5.486	4.970	5.391	6.800
r	101	1.209	3.060	1.559	1.392	.709
	$\bar{1}0\bar{1}$	2.495	2.558	2.159	1.557	1.113
r^1	$10\bar{1}$	2.156	1.170	1.519	1.254	.821
	$\bar{1}01$	1.769	2.804	2.386	1.307	.803
q	$0\bar{1}1$	.025	.022	.031	.030	.027
	$0\bar{1}\bar{1}$	.077	.024	.019	.033	-
o	$1\bar{1}1$	0.016	-		-	-
	$\bar{1}\bar{1}\bar{1}$	-	-		-	-
Total Area		56.791	57.674	48.894	49.155	61.249
Weight (gms)		0.0444	0.0486	0.0345	.0356	.0519
$K = \frac{S}{W^{2}/3}$		4.53	4.33	4.61	4.54	4.40

Table 3 (contd.)

Face		Surface Areas (sq. mms).			
		6	7	8	9
a	100	13.813	14.274	12.035	15.958
	$\bar{1}00$	15.357	14.441	11.101	15.648
p	110	8.620	5.496	2.605	4.692
	$\bar{1}10$	5.988	4.066	2.945	3.949
p^1	$1\bar{1}0$	6.449	2.952	2.596	3.729
	$\bar{1}\bar{1}0$	7.482	3.481	2.545	3.673
c	001	10.037	6.639	5.418	8.433
	$00\bar{1}$	9.978	5.992	5.242	7.550
r	101	0.979	1.834	2.017	2.609
	$\bar{1}0\bar{1}$	1.279	1.512	1.401	1.861
r^1	$10\bar{1}$	0.898	1.614	1.215	1.795
	$\bar{1}01$	0.989	1.256	2.176	3.062
q	$0\bar{1}1$	0.064	1.517	0.033	0.123
	$0\bar{1}\bar{1}$	0.073	.018	-	0.067
o	$1\bar{1}1$	0.124	.123	-	0.040
	$\bar{1}\bar{1}\bar{1}$	-	-	-	0.088
Total area		82.130	65.215	51.329	73.278
Weight		0.0803	0.0513	.0353	.0626
$K = \frac{S}{W^{2/3}}$		4.41	4.72	4.76	4.65

Mean value of K = 4.55 ± 0.12

The second assumption made by Kucharenko, that the rate of increase in weight of a crystal is proportional to the surface area introduces an error, since different faces of a crystal do not grow at the same rate as will be shown later.

The accuracy of the method is thus difficult to estimate, as both the calculated surface areas and the increases in weight recorded will be dependent upon the form of the crystals chosen for the experiments.

In the determination of the increase in weight of crystals during an experiment the crystal was cleaned before and after growth with alcohol saturated with sucrose, as has been described previously. In order to test the accuracy with which crystal weights could be reproduced, a number of dried and weighed crystals were immersed for a few minutes in a saturated sucrose solution and then removed, cleaned with alcohol and dried to constant weight. No detectable change in weight was observed, indicating that the method of cleaning with alcohol was satisfactory.

IV THE EFFECT OF RATE OF FLOW OF SOLUTION ON CRYSTALLISATION VELOCITY.

As mentioned previously, the method adopted for the investigation of this effect was to construct cells of different diameters, and connect these in series in the air thermostat. With a constant rate of flow of solution round the circuit, the velocity through the different cells may thus be varied at will. The advantage of this method is that it enables the velocity effect to be investigated under otherwise exactly comparable conditions of supersaturation and temperature of solution.

The velocity of crystallisation in stationary solution was determined in a number of experiments by suspending a crystal in the centre of a 200 ml flask, filled with solution, and immersed in the final thermostat of the apparatus.

A crystal growing under these conditions will not be in strictly stationary solution, as small convection currents inevitably arise due to the diminution in the concentration of solution near the crystal. However, on account of the slow rate of crystallisation of sucrose, and the high viscosity of the solution convection currents are very small and the conditions must approach very nearly to those in truly stationary solution. Solutions of high supersaturation cannot be investigated by this means, as spontaneous crystallisation occurs too rapidly and small crystals formed in the solution adhere to the faces of the larger crystal. The velocity of crystallisation in "stationary" solution has, therefore, not been determined for all solutions investigated.

As can be seen in Tables 4 to 10 pp. 73-79, the effect of rate of flow of solution on crystallisation velocity, has been investigated at temperatures of 30°, 40° and 50°C, at various supersaturations in each case.

In expressing the results of these experiments, the question arises as to how "rate of flow of solution" should be defined, and it is necessary to deal first with this point.

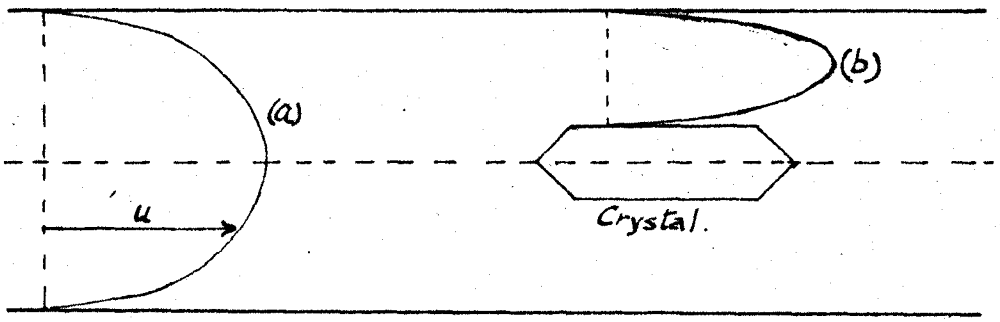
(1) Definition of Rate of Flow.

Previous investigators, when considering crystallisation from stirred solutions, appear almost without exception to have assumed that a stationary layer of solution exists on the crystal surfaces. From the hydrodynamical point of view, however, there seem to be no grounds for this assumption. It has been found experimentally in the study of the motion of fluids of small viscosity (such as air or water) around a body, that the velocity of the fluid is practically uniform except in a thin layer surrounding the body, where the velocity gradient becomes large, and the velocity falls rapidly to zero at the solid boundary. This region, which is always in steamline, or laminar flow even when the outer fluid is turbulent, has been termed the boundary layer; the definition of the thickness of the layer being to a certain extent arbitary. One method of expressing the thickness is to define it as the distance from the surface where the velocity differs by 1% from the velocity of the fluid at infinity. The thickness of the boundary layer increases with increasing viscosity of the fluid.

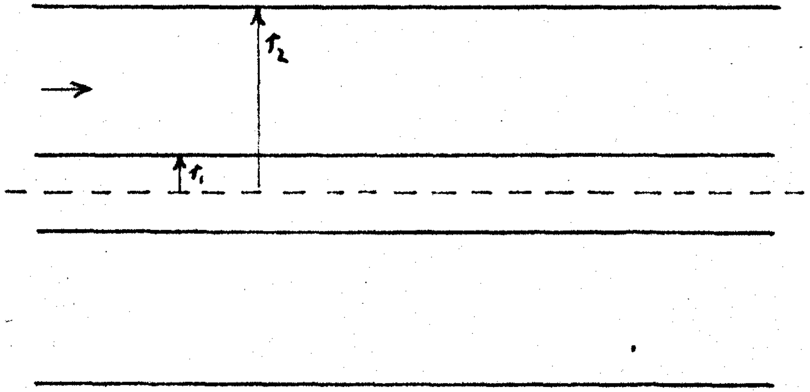
In the case of a supersaturated solution flowing past a crystal there seems to be no reason to suppose that essentially similar conditions do not hold, i.e., that the solution has finite velocities right up to the crystal faces.

The apparatus used for the present work was designed so that some estimate of solution velocities near the crystal could be made. As a rigorous treatment of the flow of solution round a body such as sucrose crystal did not seem possible, various simplifying assumptions were made.

Referring to Figure 15., the velocity distribution of the solution flowing in the cell before reaching the crystal will be of the form shown by curve (a) at the left. On the crystal



— FIGURE 15 —



— FIGURE 16 —

surface, the velocity is zero, and the velocity distribution takes on the form shown by curve (b). With the rates of flow of solution employed in the experiments, flow was streamline in all cases.

To calculate approximately the velocity distribution round the crystal, the following assumptions were made:

1) The disturbing effect on flow of the thin wire crystal holder was neglected.
2) The crystal was assumed to have circular cross-section instead of that shown in Fig. 7b.
3) The crystal was taken to be sufficiently long for a steady velocity distribution to be reached on its surface.

Obviously at the front end of the crystal the flow will not immediately reach a steady state, and at the rear end will also be disturbed. However, making these assumptions to obtain an approximate solution, the problem reduces to one of flow through an annular space formed between the outer tube and a co-axial cylinder, as shown in Figure 16.

Measuring distances from the centre axis, it may readily be shown that the velocity of solution at any point at distance r from the axis is given by :

$$u = \frac{p_1 - p_2}{4\eta l}\left(r^2 - r_1^2 - \frac{r_2^2 - r_1^2}{\log \frac{r_2}{r_1}} \cdot \log \frac{r}{r_1}\right) \text{——} (1)$$

where:

u = velocity of solution

$\frac{p_1 - p_2}{l}$ = pressure drop over length l measured along the axis.

η = viscosity

r_1 = radius of centre cylinder

r_2 = " " outer "

The volume flowing per second, Q, is given by the integral:

$$Q = 2\pi\int_{r_1}^{r_2} u r . dr = \frac{2\pi(p_1 - p_2)}{4\eta l}\int_{r_1}^{r_2}\left(r^2 - r_1^2 - \frac{r_2^2 - r_1^2}{\log \frac{r_2}{r_1}} \log \frac{r}{r_1}\right) r . dr$$

$$= \frac{\pi(p_1 - p_2)}{8\eta l}\left(r_1^4 - r_2^4 + \frac{(r_2^2 - r_1^2)^2}{\log_e \frac{r_2}{r_1}}\right) \text{——} (2).$$

Eliminating $\frac{p_1 - p_2}{\eta l}$ from (1) and (2)

$$u = \frac{2Q}{\pi}\left\{\frac{r^2 - r_1^2 - \frac{r_2^2 - r_1^2}{\log \frac{r_2}{r_1}} \cdot \log \frac{r}{r_1}}{r_1^4 - r_2^4 + \frac{(r_2^2 - r_1^2)^2}{\log_e \frac{r_2}{r_1}}}\right\} \qquad (3)$$

i.e. U is given as a function of r, in terms of the known values of Q, and the radii of the two cylinders, r_1 and r_2. It can be seen that U becomes zero at $r = r_1$ and r_2. Maximum velocity is reached at the point

$$r = \sqrt{\frac{r_2^2 - r_1^2}{2\log_e \frac{r_2}{r_1}}}$$

The form of equation (3) is such that if U is plotted against r, the curve is very nearly linear for small values of r up to about $(r_1 + 0.01)$ cms.; i.e. $\frac{du}{dr}$ is sensibly constant. Thus if the velocity gradient at the surface of the inner cylinder, $\frac{du}{dr}$ at $r = r_1$, is found, it will serve to define the flow in the immediate vicinity of the cylinder.

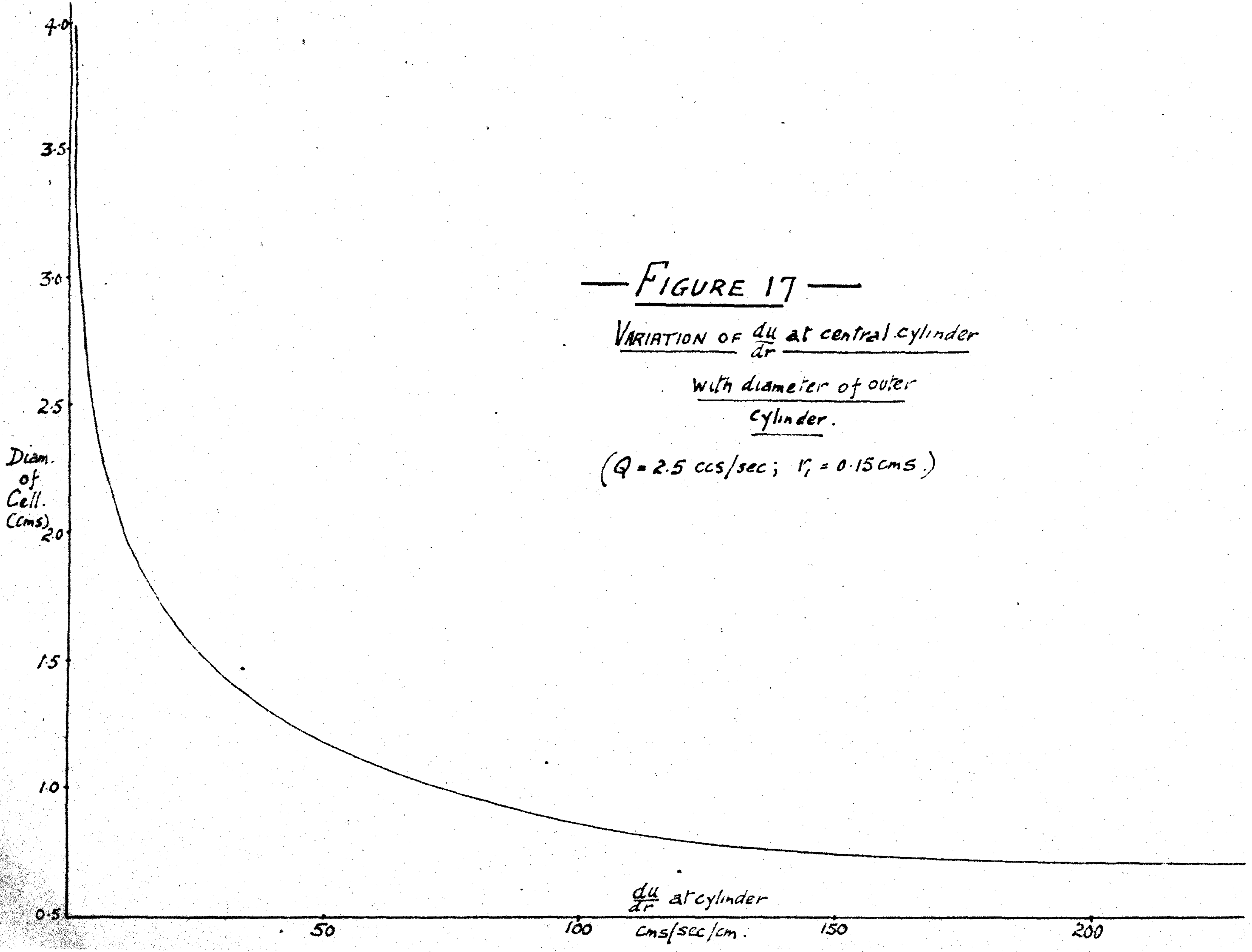
Differentiating equation (3),

$$\left(\frac{du}{dr}\right)_{r=r_1} = \frac{2Q}{\pi}\left\{\frac{2r_1 - \frac{r_2^2 - r_1^2}{r_1 \log_e \frac{r_2}{r_1}}}{r_1^4 - r_2^4 + \frac{(r_2^2 - r_1^2)^2}{\log_e \frac{r_2}{r_1}}}\right\}. \qquad (4)$$

On account of the simplifying assumptions that have been made, this equation will not hold strictly when applied to a crystal centered in a tube, but when comparing the flow of solution past similar crystals in cells of different diameters, the calculated values of $\frac{du}{dr}$ at the crystal should give at least a relative measure of velocity differences. The graph, Figure 17 shows how $\frac{du}{dr}$ at the surface of the centre cylinder alters with diameter of the outer tube, taking the central cylinder 0.3 cms. diameter and a rate of flow of solution of 2.5 ccs/second. The value of $\frac{du}{dr}$ falls asymptotically to zero as the outer tube diameter is increased to infinity, and rises rapidly as the diameter is decreased below about 1.5 cms.

(2) Experimental Results.

Tables 4 to 10 following show the effect of rate of flow of solution on growth rates of different faces. Tables 4 to 6 are for solutions at 30°C at different supersaturations, Tables 7 to 8 for 40°C and Tables 9 to 10 for 50 C. At the top of each main vertical column is given the internal diameter of the cell used, and the value of $\frac{du}{dr}$ at the crystal, calculated from equation (4). It will be seen (particularly in Tables 7 to 10) that a wide range



— FIGURE 17 —

VARIATION OF $\frac{du}{dr}$ at central cylinder with diameter of outer cylinder.

($Q = 2.5$ ccs/sec; $r_1 = 0.15$ cms.)

of velocity gradients is covered. Measurement of the growth rates of the r $\{101\}$ faces was not carried out in the first three experiments, Tables 4 to 6, and these contain the results for only 10 faces of the crystal. In the remainder of the tables, the rates for the r faces are included.

It will be seen from the tables that the two faces of every form grow at the same rate within experimental error, and accordingly mean values for the various pairs of faces are shown in the tables.

At the bottom of each column is given the overall crystallisation rate calculated by Kucharenko's method from the weights before and after growth. The rates are expressed, in conformity with Kucharenko, as mgms/m^2/ min.

The results for the growth rates of the faces are shown graphically in Figures 18-24, growth rate being plotted against velocity gradient of solution. It should be noted that ordinate and abscissa scales differ in the various graphs.

TABLE 4.

Temperature 30°C. Average radius of crystals, r_1 = 0.18 cms.

Supersaturation of solution = 4.88 gms/100 ccs.

Rate of flow of solution = 2.33 ccs/sec.

Cell radius, r_2		Stationary Soln.		1.25 cms		0.725 cms		0.525 cms	
$\frac{du}{dr}$ at crystal (cms/sec/cm)		o		4.8		24		68	
Face Symbols		Rate of Growth of Faces (mms/hour)							
			Mean		Mean		Mean		Mean
a	100	.018	.017	.022	.021	.023	.022	.022	.021
	$\bar{1}00$	.016		.020		.020		.020	
p	110	.058	.056	.058	.059	.068	.070	.067	.070
	$\bar{1}10$	.054		.059		.071		.072	
p^1	$1\bar{1}0$	.022	.022	.028	.029	.027	.030	.029	.031
	$\bar{1}\bar{1}0$	.021		.030		.032		.032	
c	001	.025	.023	.031	.031	.029	.029	.027	.029
	$00\bar{1}$	.021		.030		.029		.030	
r^1	$10\bar{1}$	.028	.027	.038	.036	.036	.036	.038	.037
	$\bar{1}01$	.026		.033		.036		.036	
Overall cryst. velocity mgms/m^2/min.		-		860		950		930	

TABLE 5.

Temperature 30°C. Average radius of crystals r_1 = 0.18 cms.
Supersaturation of solution = 8.47 gms/100 ccs.
Rate of flow of solution = 2.54 ccs/sec.

Cell radius r_2		1.25 cms		0.725 cms.		0.525 cms.	
$\frac{du}{dr}$ at crystal (Cms/sec/cm)		5.2		26		73	
Face Symbols.		Rate of Growth of Faces (mms/hour)					
			Mean		Mean		Mean
a	100	.035	.036	.037	.039	.036	.038
	$\bar{1}00$	.037		.040		.040	
p	110	.103	.106	.118	.123	.125	.122
	$\bar{1}10$	.109		.127		.119	
p^1	$1\bar{1}0$	.046	.044	.040	.046	.044	.045
	$\bar{1}\bar{1}0$	.042		.052		.046	
c	001	.044	.043	.040	.038	.044	.043
	$00\bar{1}$	.042		.036		.042	
r^1	$10\bar{1}$	.059	.058	.059	.057	.059	.058
	$\bar{1}01$	.057		.054		.057	
Overall cryst. velocity mgms/m^2/min.		1620		1620		1650	

TABLE 6.

Temperature 30°C. Average radius of crystals, r_1 = 0.18 cms.
Supersaturation of solution = 9.31 gms/100 ccs.
Rate of flow of solution = 2.51 ccs/sec.

Cell radius r_2		Stationary Soln.		1.25 cms		0.525 cms	
$\frac{du}{dr}$ at crystal (Cms/sec/cm)		o		5.2		73	
Face Symbols		Rate of Growth of Faces (mms/hour)					
			Mean		Mean		Mean
a	100	.028	.028	.038	.038	.041	.042
	$\bar{1}00$	.027		.038		.042	
p	110	.078	.076	.128	.127	.131	.129
	$\bar{1}10$	.073		.125		.127	
p^1	$1\bar{1}0$	.031	.032	.044	.044	.048	.047
	$\bar{1}\bar{1}0$	.033		.044		.045	
c	001	.024	.025	.039	.039	.047	.046
	$00\bar{1}$	.026		.039		.045	
r^1	$10\bar{1}$	.054	.058	.062	.062	.086	.092
	$\bar{1}01$	.062		-		.098	
Overall crys. velocity mgms/m^2/min.		981		1850		1900	

TABLE 7.

Temperature 40°C. Average radius of crystals r_1 = 0.15 cms.
Supersaturation of Solution = 4.83 gms/100 ccs.
Rate of flow of solution = 2.41 ccs/sec.

Cell radius r_2		1.99 cms		0.525 cms		0.37 cms	
$\frac{du}{dr}$ at crystal (Cms/sec/cm)		1.5		66		222	
Face Symbols		Rate of Growth of Faces (mms/hour)					
			Mean		Mean		Mean
a	100	.043	.044	.051	.049	.049	.050
	$\bar{1}00$	.045		.046		.051	
p	110	.125	.130	.198	.188	.184	.184
	$\bar{1}10$	.135		.178		-	
p^1	$1\bar{1}0$	.042	.046	.067	.068	.067	.067
	$\bar{1}\bar{1}0$	.050		.068		-	
c	001	.055	.056	.061	.061	.063	.062
	$00\bar{1}$	.057		.061		.061	
r^1	$10\bar{1}$	.073	.079	.084	.087	.089	.088
	$\bar{1}01$	.084		.090		.087	
r	101	.066	.066	.079	.065	.085	.080
	$\bar{1}0\bar{1}$	.066		.051		.075	
Overall crys. velocity mgms/m^2/min.		1850		-		2250	

TABLE 8.

Temperature 40°C. Average radius of crystals, r_1 = 0.15 cms.

Supersaturation of solution = 8.97 gms/100 ccs.

Rate of flow of solution = 2.50 ccs/sec.

Cell radius r_2		Stationary Soln.		1.99 cms		0.37 cms	
$\frac{du}{dr}$ at crystal (Cms/sec/cm)		o		1.6		231	
Face Symbols.		Rate of Growth of Faces (mms/hour)					
			Mean		Mean		Mean
a	100	.057	.060	.081	.082	.102	.103
	$\bar{1}00$	.063		.083		.103	
p	110	.178	.167	.289	.269	.346	.355
	$\bar{1}10$	.156		.250		.364	
p^1	$1\bar{1}0$	.065	.081	.119	.108	.154	.155
	$\bar{1}\bar{1}0$	.097		.097		.155	
c	001	.079	.076	-	.100	.133	.134
	$00\bar{1}$	.073		.100		.134	
r^1	$10\bar{1}$	.102	.102	.155	.141	.190	.188
	$\bar{1}01$	.101		.126		.185	
r	101	.090	.093	.143	.143	.192	.194
	$\bar{1}0\bar{1}$	.096		-		.195	
Overall cryst.velocity mgms/m^2/min.		2500		3670		4900	

TABLE 9.

Temperature 50°C. Average radius of crystals r_1 = 0.15 cms.

Supersaturation of solution = 3.96 gms/100 ccs.

Rate of flow of solution = 2.31 ccs/sec.

Cell radius r_2		1.99 cms		0.625 cms		0.37 cms	
$\frac{du}{dr}$ at crystal. (Cms/sec/cm)		1.4		64		213	
Face Symbols.		Rate of Growth of Faces (mms/hour)					
			Mean		Mean		Mean
a	100	.071	.069	.078	.080	.083	.084
	$\bar{1}00$	.067		.081		.084	
p	110	.151	.168	.257	.264	.250	.265
	$\bar{1}10$	.184		.271		.280	
p^1	$1\bar{1}0$	.094	.090	.097	.090	.100	.097
	$\bar{1}\bar{1}0$	.085		.083		.093	
c	001	.071	.074	.104	.104	.104	.100
	$00\bar{1}$	.076		.104		.096	
r^1	$10\bar{1}$	.103	.105	.138	.140	.151	.150
	$\bar{1}01$	.106		.142		.149	
r	101	.091	.091	.140	.130	.160	.140
	$\bar{1}0\bar{1}$	.090		.120		.120	

TABLE 10.

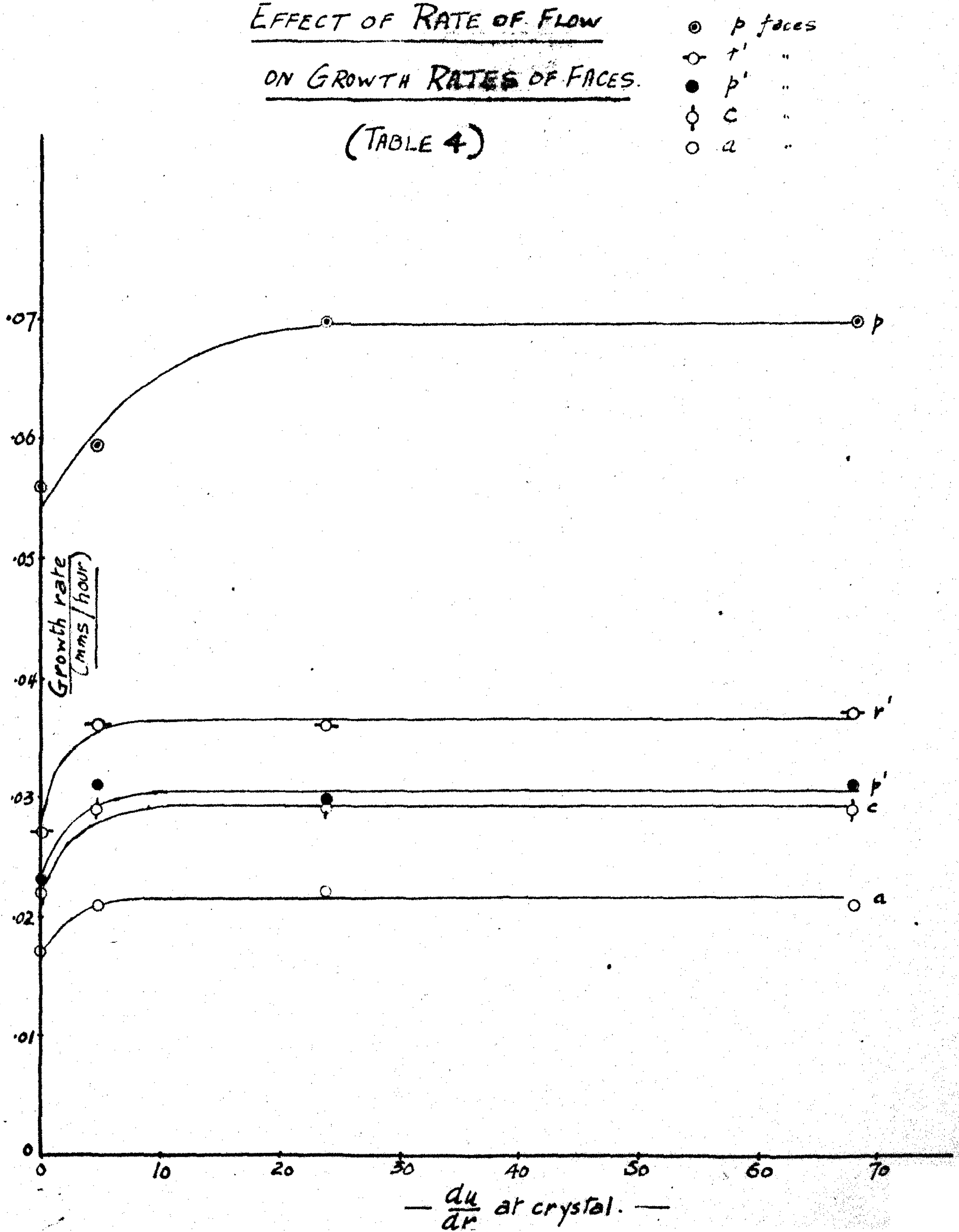
Temperature 50°C. Average radius of crystals r_1 = 0.15 cms.
Supersaturation of solution = 3.67 gms/100 ccs.
Rate of flow of solution = 2.51 ccs/sec.

Cell radius r_2		Stationary Soln.		1.99 cms		0.525 cms		0.37 cms	
$\frac{du}{dr}$ at crystal (Cms/sec/cm)		o		1.6		69		232	
Face Symbols.		Rate of Growth of Faces (mms/hour)							
			Mean		Mean		Mean		Mean
a	100	.072	.076	.101	.097	.123	.118	.124	.123
	$\bar{1}00$	.080		.093		.113		.120	
p	110	.150	.161	.263	.276	.368	.364	.395	.380
	$\bar{1}10$	.172		.288		.360		.365	
p^1	$1\bar{1}0$	.098	.094	.118	.111	.135	.130	.125	.140
	$\bar{1}\bar{1}0$	.090		.104		.125		.155	
c	001	.086	.086	.112	.123	.132	.130	.130	.132
	$00\bar{1}$	.086		.134		.128		.133	
r^1	$10\bar{1}$	.126	.126	.137	.137	.190	.183	.195	.194
	$\bar{1}01$	-		-		.176		.192	
r	101	.071	.079	.136	.136	.190	.190	.187	.194
	$\bar{1}0\bar{1}$	.087		-		-		.200	
Overall cryst. velocity mgms/m^2/min.		2644		4091		5370		5100	

FIGURE 18

EFFECT OF RATE OF FLOW ON GROWTH RATES OF FACES.

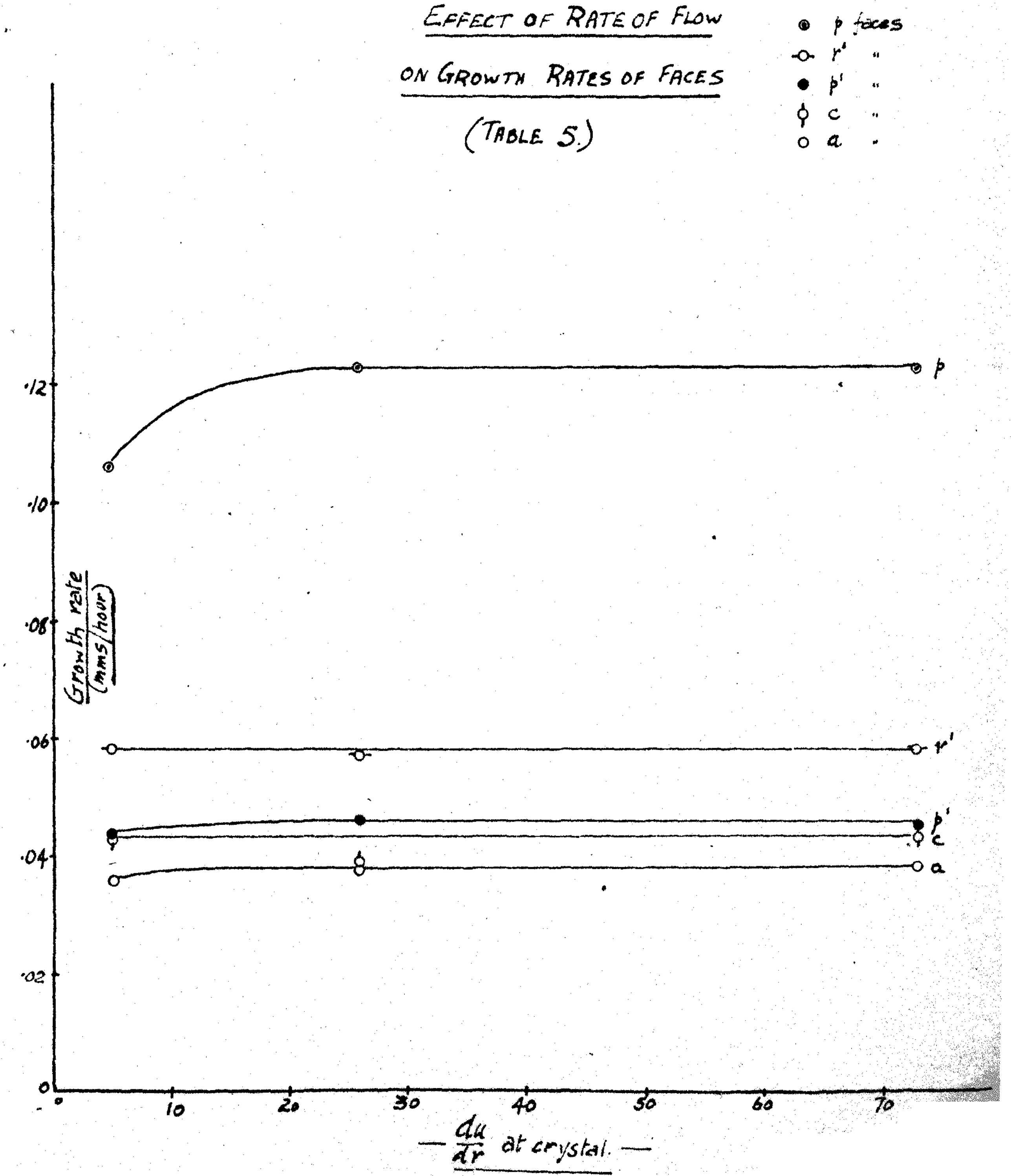
(TABLE 4)



—FIGURE 19—

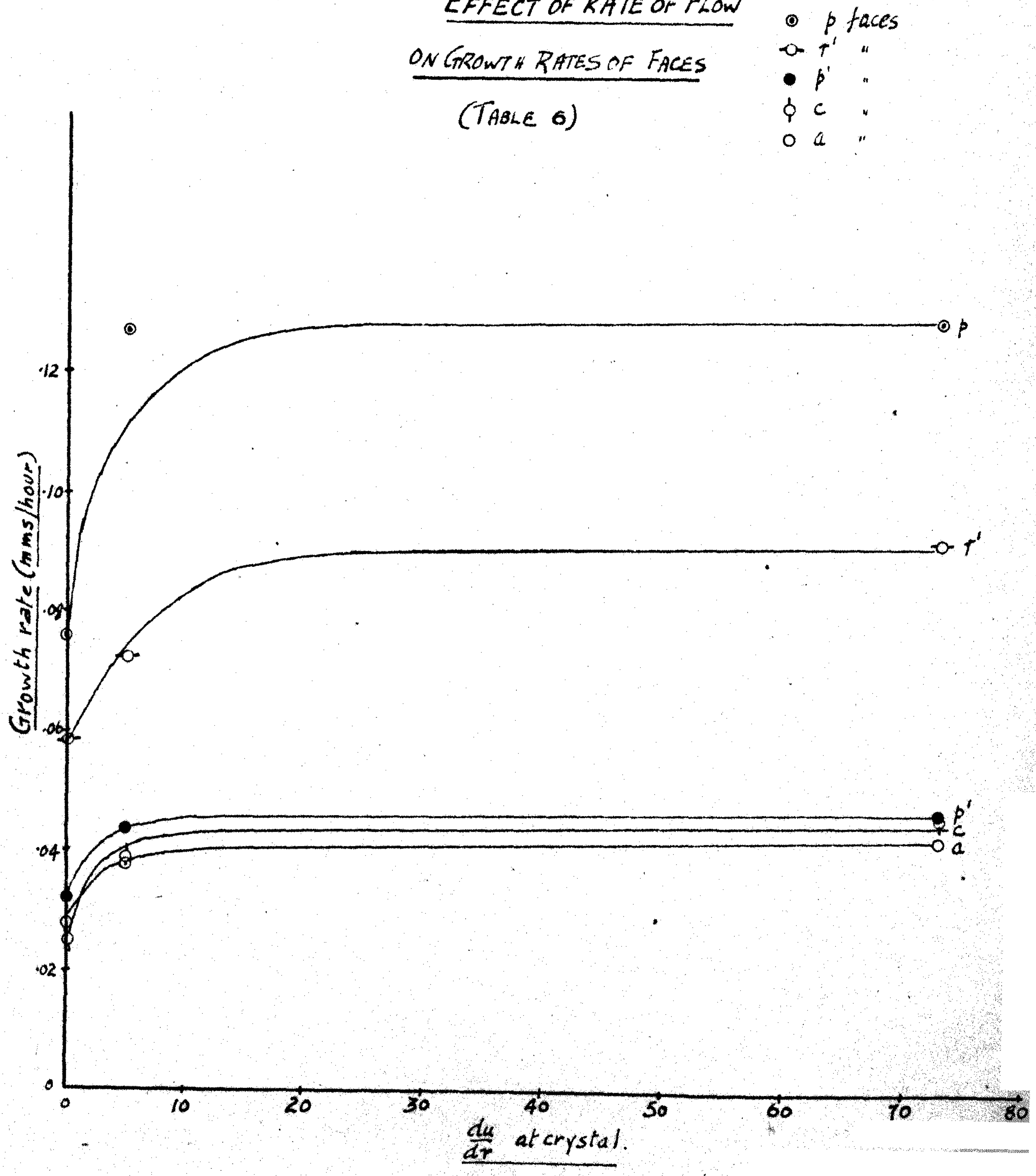
EFFECT OF RATE OF FLOW ON GROWTH RATES OF FACES

(TABLE 5.)



— FIGURE 20 —

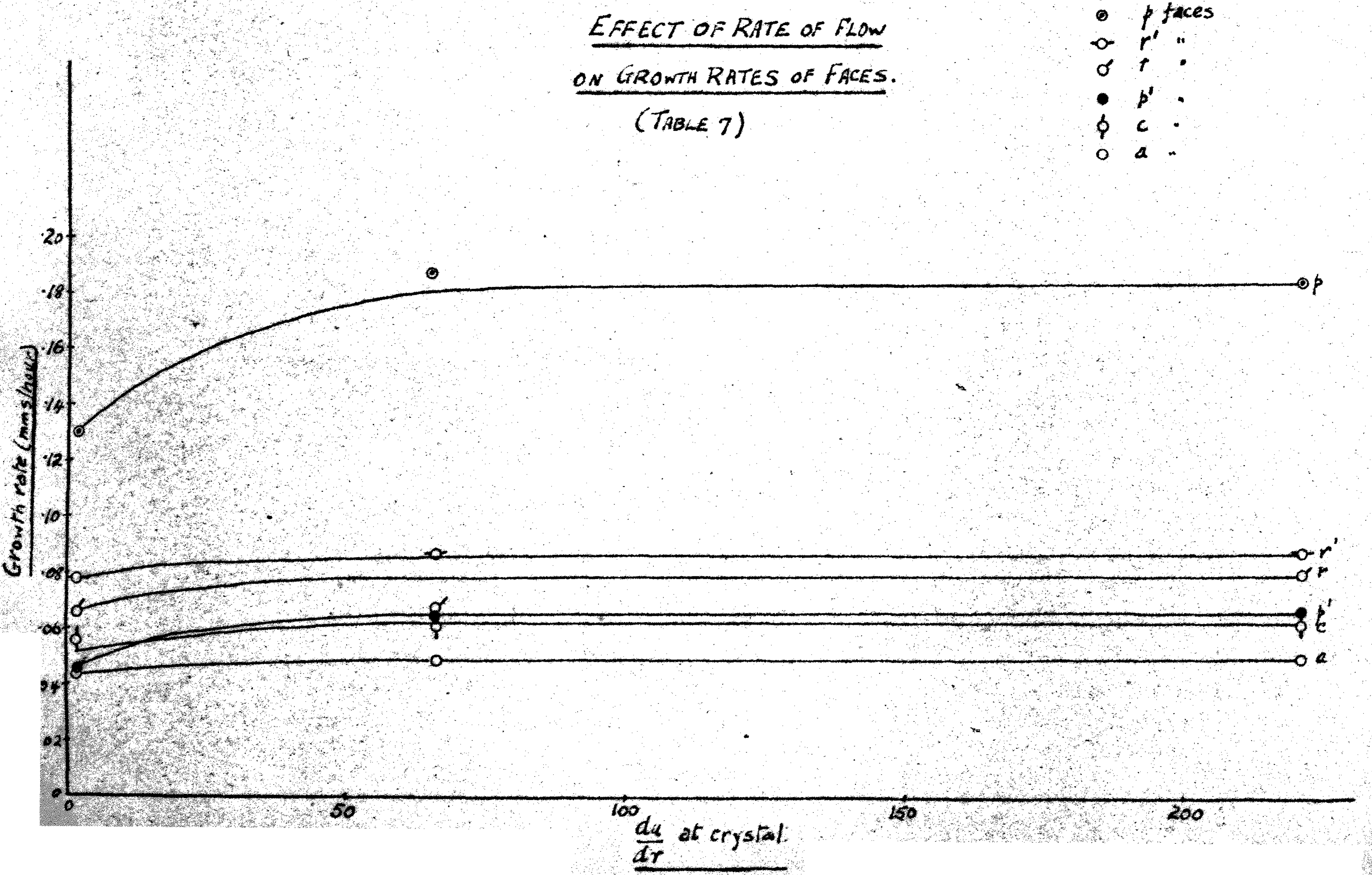
EFFECT OF RATE OF FLOW
ON GROWTH RATES OF FACES
(TABLE 6)

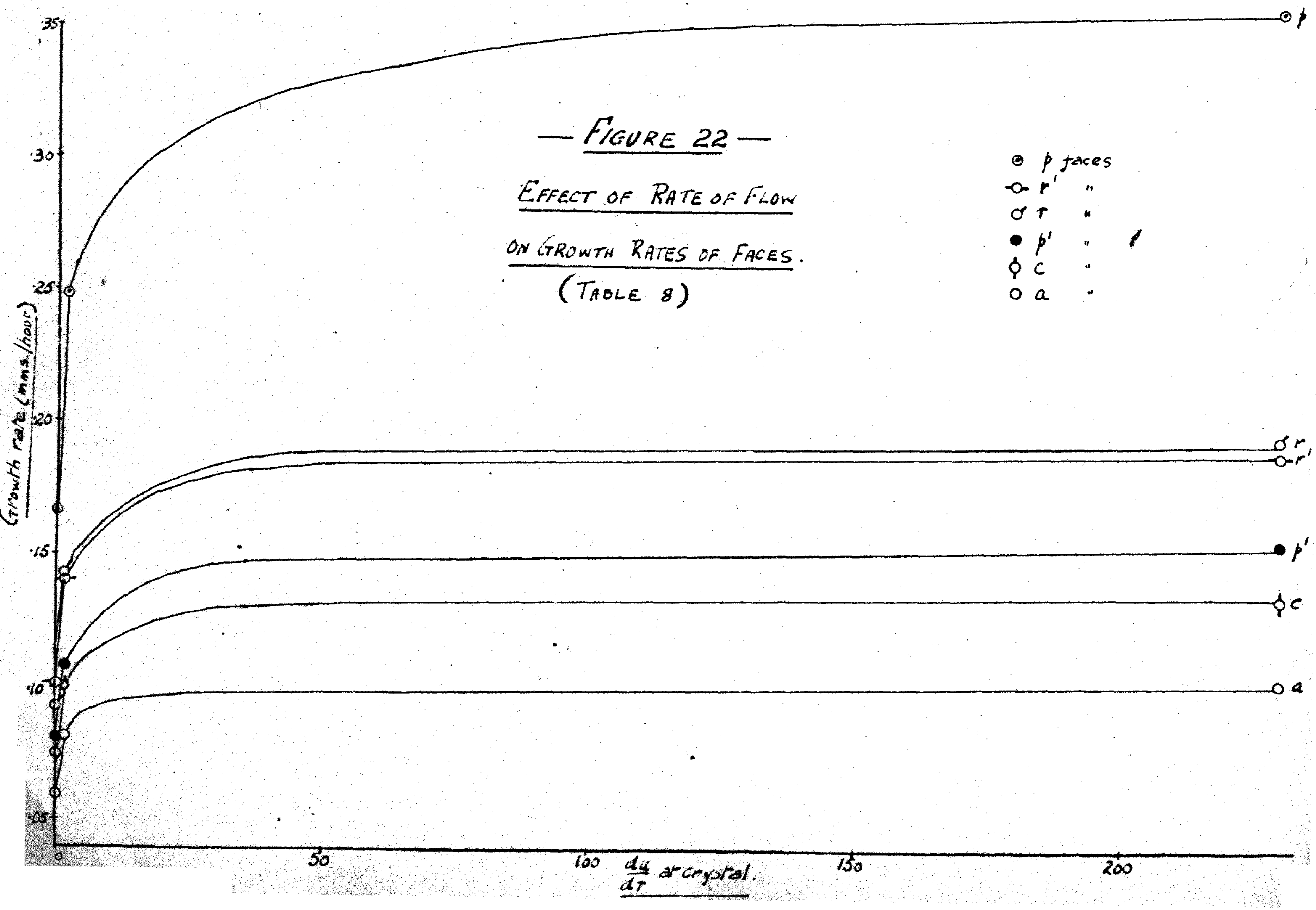


—FIGURE 21.—

EFFECT OF RATE OF FLOW ON GROWTH RATES OF FACES.

(TABLE 7)





— FIGURE 22 —

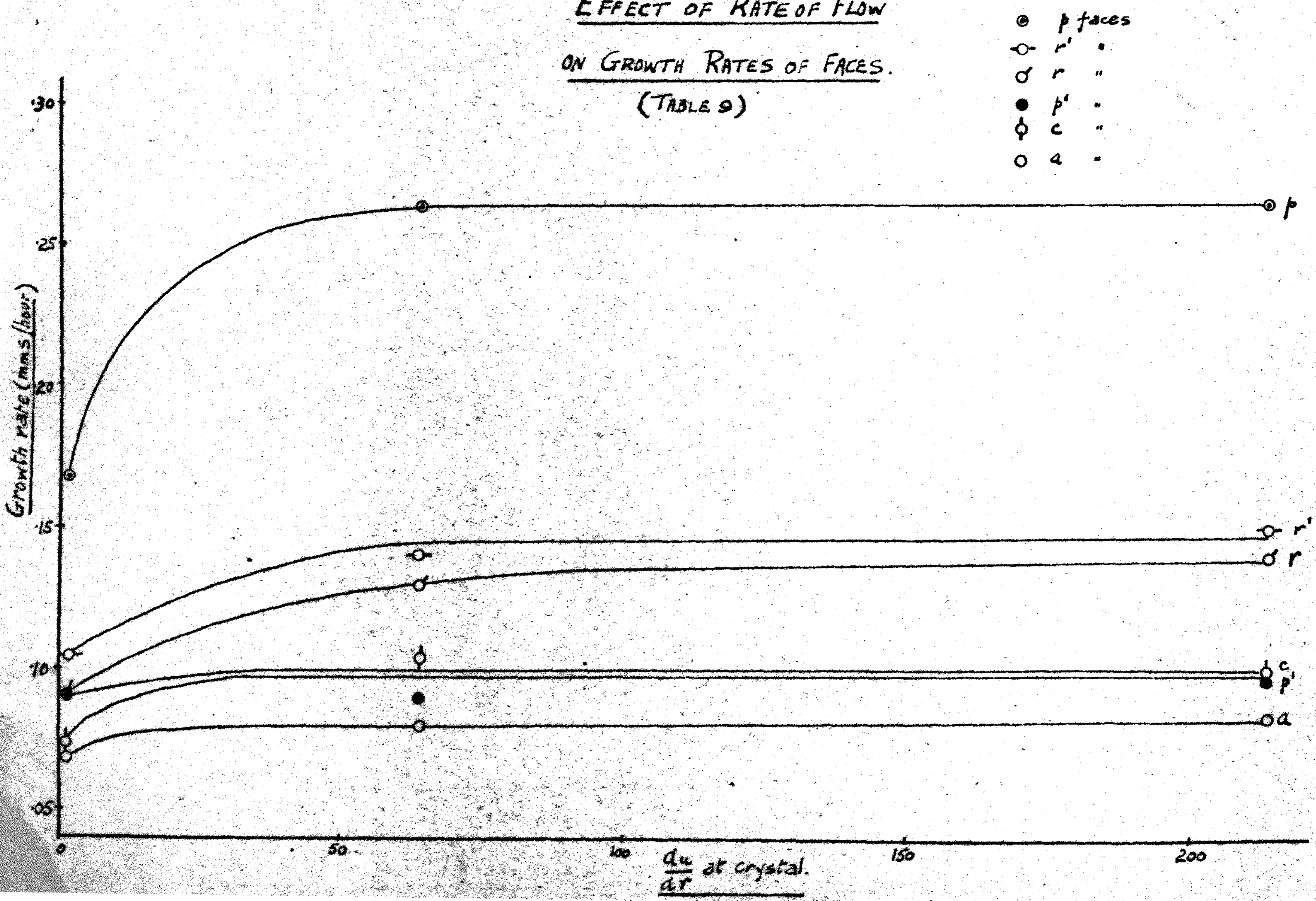
EFFECT OF RATE OF FLOW ON GROWTH RATES OF FACES.

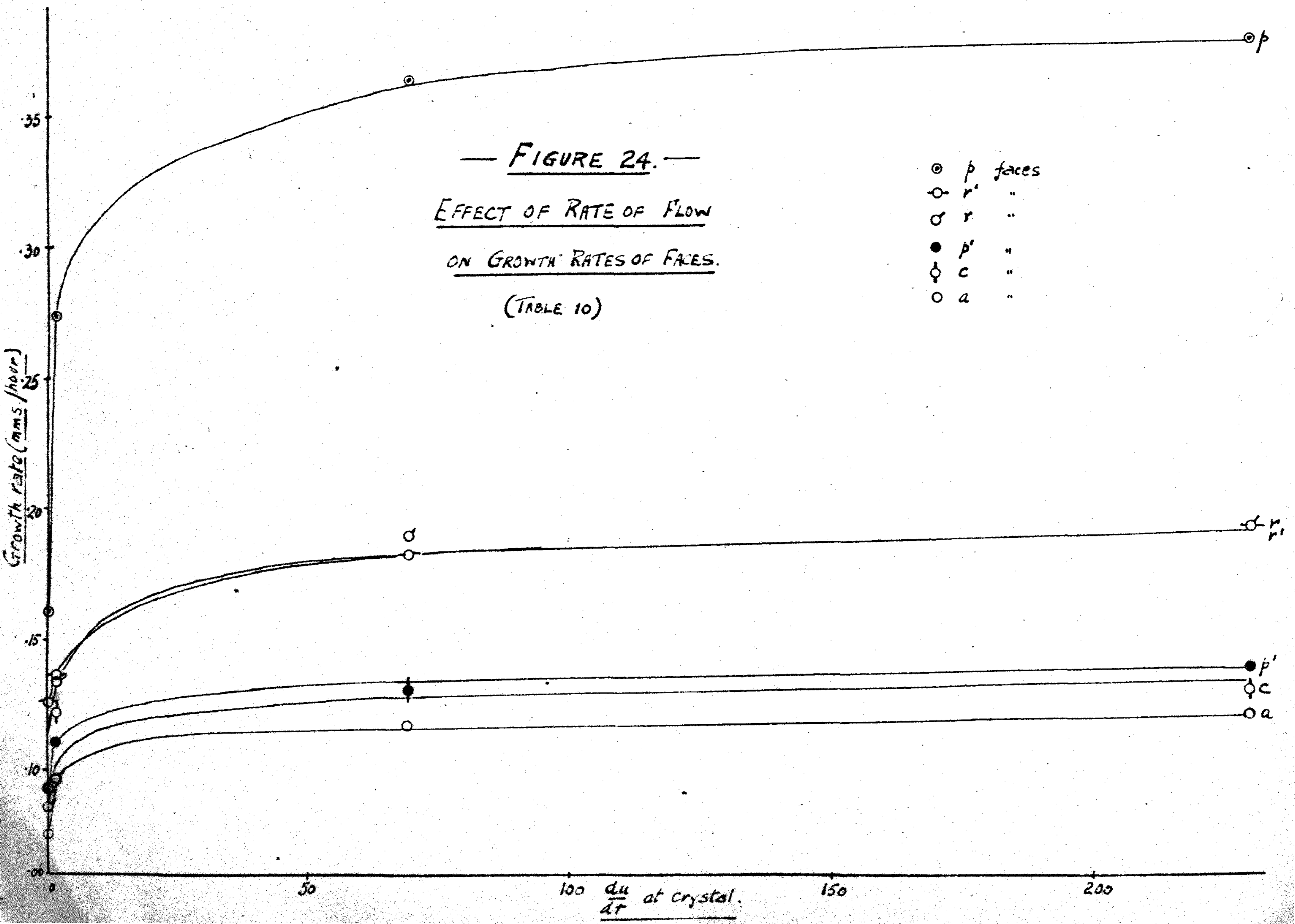
(TABLE 8)

— FIGURE 23 —

EFFECT OF RATE OF FLOW ON GROWTH RATES OF FACES.

(TABLE 9)





— FIGURE 24. —

EFFECT OF RATE OF FLOW ON GROWTH RATES OF FACES.

(TABLE 10)

(3) Discussion of Results.

It will be evident from the tables that the different faces of the crystal grow at different rates. This effect will be dealt with subsequently (see Section V) and in the present section only the effect of rate of flow of solution considered.

The tables and graphs shew that the rates of growth of the various faces increase with increasing velocity of solution to maximum values, past which further increase in velocity of solution is without effect on the growth rate within experimental error. In most cases the maximum rate is reached at quite small solution velocities.

The overall crystallisation rates, expressed as mgms/M^2/min confirm these increases in the growth rates of the individual faces,

It can be seen from the form of the curves that the effect of rate of flow of solution becomes more marked as the growth rates become higher, and in order to show this effect, the differences between the rates in stationary solution and the maximum rates for each face ($R_{max} - R_o$) have been plotted against the maximum rate, (R_{max}), in Figure 24a.

The growth rates in stationary solution were not determined in all cases, and Figure 24a includes the results of Tables 4, 6, 8, and 10. An average curve may be drawn through the points, as shown; the points are rather scattered as the difference term $(R_{max} - R_o)$ introduces an error of about ± 10%, but the trend of the curve is clear.

The results may first be considered in the light of the Nernst theory which has been outlined on p.9. It was assumed in this theory that the concentration of solution in contact with the crystal face was the saturation concentration, C_o, and that the rate of diffusion of solute across the boundary layer was the determining factor in the process.

Applying this theory to the case of sucrose consider the growth of the a $\{100\}$ faces in Table (6) where the calculated velocity gradient of solution on the face is 73 cms/sec/cm.

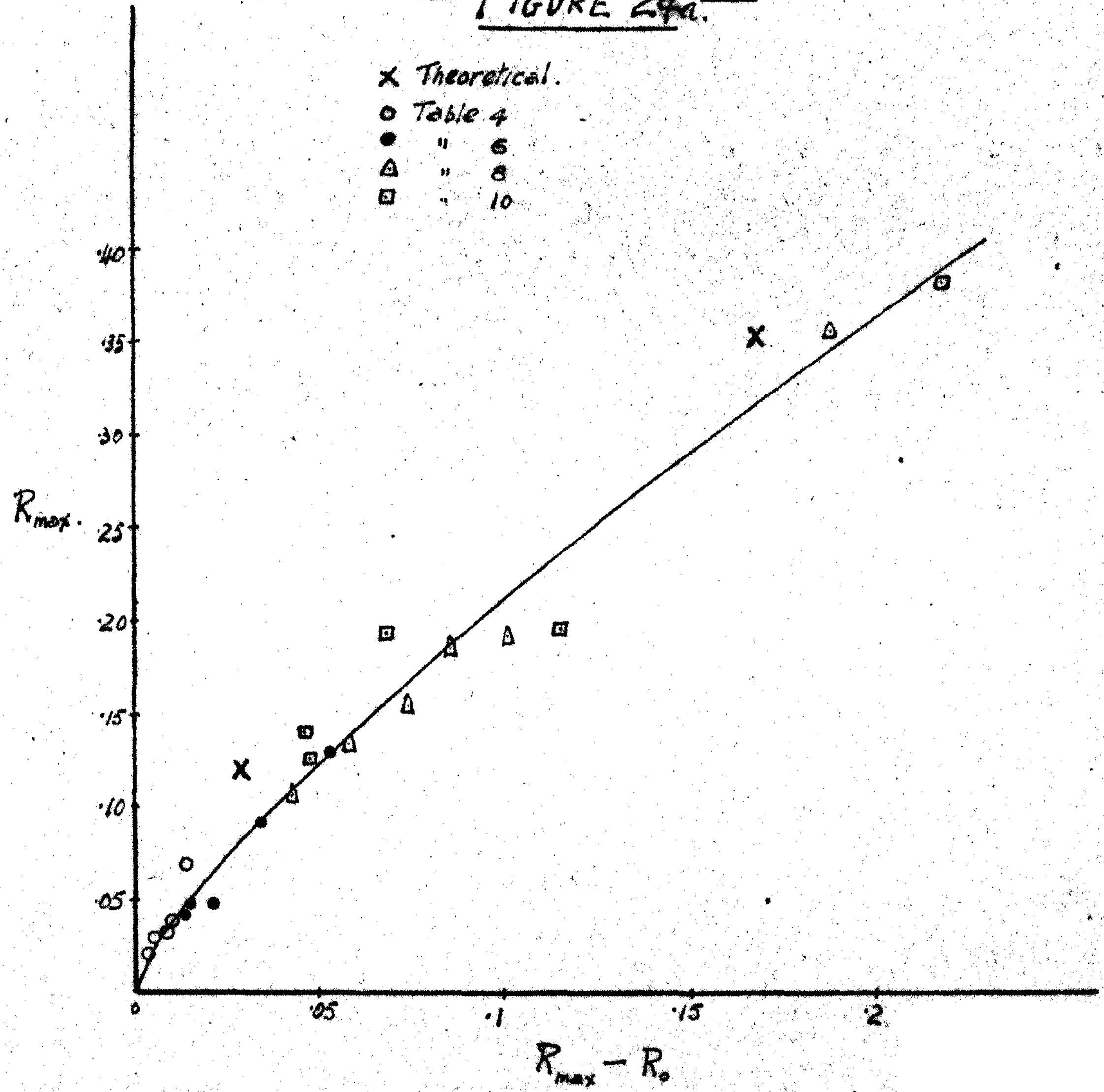
Here, Rate of growth = 0.042 mms/hour.

Supersaturation = 9.31 gms/100 ccs.

$= 0.272 \times 10^{-3}$ gm mols./cc.

If a layer of thickness d were present on the surface and if the solution in contact with the face were saturated, a concentration gradient of $\frac{0.272 \times 10^{-3}}{d}$ would exist.

FIGURE 24a.


× Theoretical.
○ Table 4
● " 6
△ " 8
⊡ " 10
R_{max}.
·40
·35
·30
·25
·20
·15
·10
·05
0
·05
·1
·15
·2
$R_{max} - R_o$

From the Fick diffusion law, for 1 sq. cm. of surface,

$$\frac{dn}{dt} = \mathcal{D} \cdot \frac{0.272 \times 10^{-3}}{d} \quad - \quad (5)$$

Where $\mathcal{D}$ = diffusion coefficient

= 0.35×10^{-5} cms.^{2}/sec at the concentration of the experiment,

$\frac{dn}{dt}$ = rate of crystallisation of the face

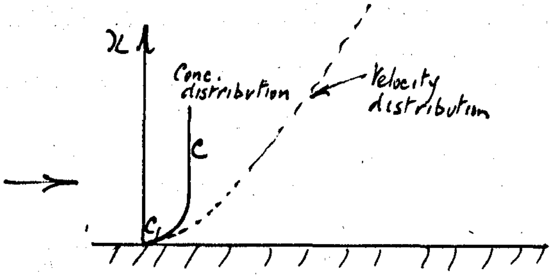
= $\frac{0.0042 \times 1.583}{342 \times 3600}$ gm. mols./sec/cm^2.

Substituting these values in equation (5) the hypothetical layer thickness, d, is found to be 0.177 cms. Even an approximate knowledge of the velocity distribution round the crystal is sufficient to show that a layer of this magnitude could not exist, and that the Nernst hypothesis cannot be applied to sucrose.

It appears that the crystallisation of sucrose is an example of a very slow reaction velocity in solution, and it would seem that in this case the actual concentration of solution in contact with the crystal approaches more nearly to the concentration in the outer solution than to the saturation concentration. The fact that crystallisation rate rises to a constant maximum value with increasing rate of flow, indicates that the concentration on the face approaches a limiting value, which must be virtually the concentration of the bulk of the solution.

It is clear, however, that diffusion does exert some influence on the crystallisation rate, since rate of flow of solution affects the process. If diffusion velocity was extremely high compared with reaction velocity at the surface, rate of flow of solution should have an inappreciable effect.

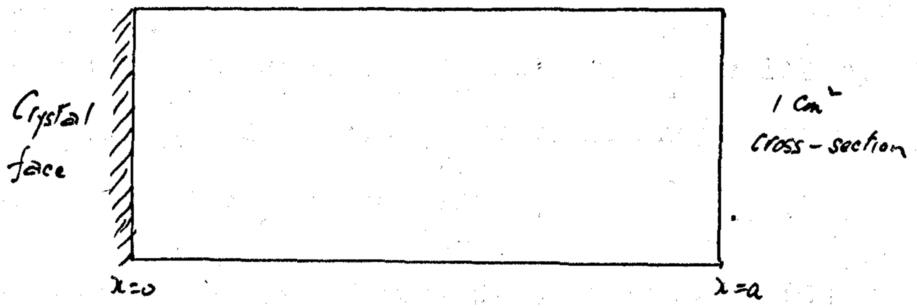
From the qualitative point of view, the conditions on the surface of a crystal in flowing solution may be regarded as follows:



Consider the face of a crystal, past which a supersaturated solution of concentration C is flowing, the velocity of the solution being zero in contact with the face, and increasing with increasing distance x. Taking any element of the solution near the face, it will be seen that sucrose is lost by diffusion in a normal direction, and gained by transfer of solution flowing parallel to the face. Under steady conditions a balance should be reached at every point and the concentration distribution should take on a definite form.

It was hoped that, since the rate of crystallisation and the approximate velocity distribution in the solution were known in each experiment, the concentration distribution in the immediate vicinity of the crystal could be calculated, and the actual concentration on the surface of the crystal found for each different solution velocity. The mathematical difficulties, however, proved considerable, and no method of solution could be found for the above case.

The question of the effect of rate of flow of solution on crystallisation velocity may be treated quantitively by taking a somewhat simplified case.



Consider a tube closed at one end, unit cross-sectional area, and length a, filled with a supersaturated solution. The end at $x = o$ is closed by a crystal face.

The growth of the face under two different conditions will be dealt with:

1) The solution is imagined to be violently stirred throughout the growth, so that at any instant the concentration is uniform from $x = o$ to $x = a$. This is analogous to the case of a solution flowing past a crystal at an infinitely fast rate.

2) The solution is allowed to remain in a stationary condition so that sucrose can approach the face only by diffusion.

Before dealing with these two cases, the conclusions drawn in the next section of the Thesis must be anticipated to a certain extent. As will be shown later, the maximum growth rate of a face bears a linear relationship to the supersaturation of solution.

i.e. $$\frac{dM}{dt} = K(C - Co) \qquad — \qquad (6)$$

where: C = concentration of the bulk of solution which must be virtually equal to the concentration on the face when the solution is flowing at relatively infinite velocity.

Co = saturation concentration.

$\frac{dM}{dt}$ = rate of crystallisation of the face which may be expressed as gms sucrose/cm^2/sec.

The K. values for the different faces have been evaluated, and are given in Section V.

Case 1. Stirred Solution.

Let the initial concentration of the solution in the vessel be C_1 gms/cc, and let Co be the saturation concentration.

$$\text{Let} \quad C_1 - C_o = \phi_1$$

As stated above, the rate of crystallisation of the face will be given at any instant by:

$$\frac{dM}{dt} = K(C - Co) = K\phi \qquad \text{—} \qquad (7)$$

The crystallisation of an amount M of sucrose lowers the concentration of the solution.

If ϕ is the ~~concentration~~ supersaturation at any time, then

$$\phi a = \phi_1 a - M$$

or
$$\phi = \phi_1 - \frac{M}{a} \qquad — \qquad (8)$$

Substituting this value of ϕ in equation (7)

$$\frac{dM}{dt} = K(\phi_1 - \frac{M}{a})$$

or
$$\frac{dM}{dt} + \frac{K}{a} M = K\phi_1 \qquad — \qquad (9)$$

The solution of this differential equation is:

$$M = \phi_1 a + Be^{-\frac{k}{a} t}$$

where B is a constant.

From the initial conditions, $M=o$ when $t=o$, $B = -\phi_1 a$, and the equation becomes

$$M = \phi_1 a (1 - e^{-\frac{k}{a} t}) \qquad — \qquad (10)$$

Applying this to a numerical example,

Let: $a = 20$ cms

$$\left.\begin{aligned} C_1 &= 1.0284 \text{ gms/cc} \\ C_o &= 0.9384 \text{ " "} \end{aligned}\right\} \phi_1 = 0.0900 \text{ gms/cc.}$$

$K = 1.761 \times 10^{-4}$, where the rate of crystallisation is expressed as gms sucrose crystallised per cm^2 per sec, and supersaturation is expressed as gms/cc.

$t = 1$ hour $= 3600$ secs.

Then after the lapse of 1 hour, the weight of sucrose crystallised will be

$$M = 0.09 \times 20 \left(1 - e^{-\frac{1.761 \times 10^{-4} \times 3600}{20}} \right)$$

$$= 0.0562 \text{ gms.}$$

This may be expressed as mms. growth, by dividing by the density of sucrose, 1.583., giving

$$G = 0.355 \text{ mms.}$$

If, with the same conditions as before the K value of the face was only one third of that previously taken, i.e , 0.587×10^{-4} the growth during the first hour would be

$$M = 0.0189 \text{ gms}$$

and the corresponding growth in mms.,

$$G = 0.120 \text{ mms.}$$

Case 2. Stationary Solution.

For the diffusion of sucrose through the tube, the second law of Fick may be applied:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad \text{— (11)}$$

Where C = concentration

and D = diffusion coefficient.

To simplify the solution of this differential equation it was assumed as a first approximation that the concentration of solution at the face of the growing crystal is sensibly constant during the first hour of growth.

Let the concentration at the face be C_f and as before, let the initial concentration be C_i .

The equation has then to be solved subject to the boundary conditions:

$x = o$, $C = C_f$ (constant)

$x = a$ $\frac{\partial c}{\partial x} = o$, since there is no passage of solute at the end.

$t = o$, $C = C_i$ for all values of x

The solution of the equation when subject to these boundary conditions is:

$$C = C_f + \frac{4}{\pi}(C_i - C_f)\left\{ \sin\frac{\pi x}{2a} e^{-\frac{\pi^2 Dt}{4a^2}} + \frac{1}{3}\sin\frac{3\pi x}{2a} e^{-\frac{9\pi^2 Dt}{4a^2}} + \right.$$

$$\left. + \frac{1}{5}\sin\frac{5\pi x}{2a} e^{-\frac{25\pi^2 Dt}{4a^2}} + \ldots \text{etc} \right\} \quad \text{— (12)}$$

After the lapse of a given time t, the amount of sucrose remaining in the tube will be given by the integral

$$\int_0^a C\,dx.$$

or the amount M, which has been removed from the tube during that time will be:

$$M = a\,C_i - \int_0^a C\,dx$$

$$= aC_i - C_f\int_0^a dx - \frac{4}{\pi}(C_i - C_f)\int_0^a \left(\sin\frac{\pi x}{2a}\, e^{-\frac{\pi^2 Dt}{4a^2}} + \frac{1}{3}\sin\frac{3\pi x}{2a}\, e^{-\frac{9\pi^2 Dt}{4a^2}} + \ldots etc \right) dx$$

Carrying out this integration with respect to x,

$$M = aC_i - aC_f - \frac{4}{\pi}(C_i - C_f)\left\{ \frac{2a}{\pi} e^{-\frac{\pi^2 Dt}{4a^2}} + \frac{2a}{9\pi} e^{-\frac{9\pi^2 Dt}{4a^2}} + \ldots etc \right\}$$

— (13)

Applying this equation to the case of the tube, consider the growth during the first hour (i.e. $t = 3600$ secs.), and let a, C_1 and Co have the same values as in Case 1. D, the diffusion coefficient has a value of 0.45×10^{-5} cm^2/sec at the given concentration.

Substituting these known values in equation (13) and taking the series to six terms, an expression for M in terms of the concentration at the face C_f is obtained

$$M = 0.70275 - 0.68334\ C_f \quad \text{---} \quad (14)$$

Now it is known that if the concentration at the face were C_f, the amount of sucrose crystallised during the period would be

$$M = K \times 3600\ (C_f - Co) \quad \text{---} \quad (15)$$

And if $K = 1.761 \times 10^{-4}$, and $Co = 0.9384$

$$M = 1.761 \times 10^{-4} \times 3600\ (C_f - 0.9384) \quad \text{---} \quad (16)$$

C_f may be eliminated from equations (14) and (16) to find the value of M, giving

$$M = 0.0296 \text{ gms.}$$

The corresponding growth of the face would then be

$$G = 0.187 \text{ mms.}$$

Again, as before, if K has a lower value of 0.587×10^{-4}, substitution in equation (16) and elimination of C_f will give

$$M = 0.0145 \text{ gms}$$

and $$G = 0.092 \text{ mms.}$$

These results may be shown as follows:

Growth of Faces (mms).

Stationary Solution	Stirred Solution	Difference
0.187	0.355	0.168
0.092	0.120	0.028

The two points obtained by plotting the differences against the maximum growths are shown on the experimental graph, Figure 24a 25. It can be seen that the theoretical values are of the same order as the experimental. The considerations given above seem, therefore, to explain satisfactorily the observed differences in rates of growth due to velocity of flow of solution. Close agreement would not be expected. In the experimental determination of crystallisation rates in stationary solution convection currents will have some effect, and furthermore the value of D the diffusion coefficient taken for the theoretical calculation is doubtful, as it has been based on Öholms determinations, extrapolated to the required concentration.

Due to the experimental method used by Öholm (36) involving diffusion from concentrated to dilute solution, the value of D is almost certainly overestimated.

It is considered, however, that the agreement obtained is sufficient to show that the observed increases in crystallisation rate are of the order to be expected from diffusion considerations.

Comparison of results with those of Savinov.

Savinov's results on the effect of stirring on crystallisation have been mentioned previously, p. 6 . The following crystallisation rates, expressed by Kucharenko's method as mgms/m^2/min were reported (3).

Solution 50°C. Conc. = 72.97 gms (100 gms solution.

$(C-C_0)$, calculated, = 1.41 gms/100 ccs.

R.P.M. of Stirrer	Rate of Cryst. in mgms/m^2/min.	
0	443	
30	566	
90	2518	
115	3044	Avge = 2980
220	2956	
340	2938	

No increases of even approximately this magnitude have been obtained during the present work. The results may be considered as follows:

The maximum rate of crystallisation observed was 2980 mgms/ m^2/min. Thus as an approximation, the overall rate for the crystal is 0.497×10^{-5} gms/cm^2/sec, in a solution of supersaturation 0.0141 gms/cc.

Hence the overall velocity constant~~s~~,

$$K = \frac{0.497 \times 10^{-5}}{0.0141} = 3.52 \times 10^{-4}$$

Applying the methods of calculation given previously, it is found that the rate of crystallisation in stationary solution would be expected to be a little less than one half that obtained with rapid stirring. The figure reported by Savinov for stationary solution is about one seventh of the maximum rate, and the results seem therefore to be of rather doubtful accuracy.

V THE EFFECT OF SUPERSATURATION AND TEMPERATURE OF SOLUTION ON CRYSTALLISATION VELOCITY

It has been shown in the last section that the growth rates of the various faces of the sucrose crystal increase to constant maximum values as the rate of flow of solution is increased. The discussion showed that the increases observed were consistant with the assumption that at sufficiently high solution velocities the concentration of solution in contact with the crystal face reaches the concentration of the bulk of solution.

In determining the effect of supersaturation of solution on crystallisation velocity, the maximum velocities should therefore be compared, i.e., the values found for the flat portion of the rate of growth/rate of flow of solution curve.

The effect of supersaturation of solution on the growth rates of the faces, at temperatures of 25, 30, 40,,50 and 60°C. is shown in Tables 11 to 15.

All figures given in the tables are the maximum growth rates in the various solutions. The tables for 30, 40 and 50°C. include the maximum values for the different faces obtained during the investigation of the effect of rate of flow of solution and given previously in Tables 4 to 10. The full velocity of crystallisation/rate of flow curves were not determined in the other cases, as the data that had already been obtained was sufficient to enable the "critical rate of flow" to be estimated for the other solutions. In carrying out these experiments a rate of flow well in excess of the critical rate was employed, to ensure that a maximum growth rate would be obtained.

At the top of each table is given the saturation concentration at the temperature of the experiments. The first column of the table shows the actual concentration of the solution used in gms per 100 gms solution, while the next two give respectively the calculated supersaturation figures $C - C_o$, and the Claasen ratios. Overall crystallisation rates expressed by Kucharenko's method in mgms/m^2/min., are recorded in the last column. These values were not determined at 25°C. Growth rates of the faces are expressed throughout in mms./hour.

The results for the growth rates of faces are shown graphically in Figures 25 to 29, plotting supersaturation $(C - Co)$ against the mean rate for each pair of faces. The overall crystallisation rates have been plotted in Figure 30 (heavy lines), the dotted lines being Kucharenko's results (2) at the various temperatures, recalculated to the corresponding supersaturation, $(C - C_o)$, figures. In the tables given in Kucharenko's paper, supersaturations are expressed as the ratios of concentration, in gms per 100 gms solution, Herzfeld's solubility figures being taken for the saturation concentrations. The writer's solubility figures have been used in the recalculation of Kucharenko's supersaturations.

Referring first to the growth rates of individual faces, Figures 25 to 29, it will be seen that within the limits of experimental error straight lines are obtained for each face. The accuracy is somewhat lower at the higher temperatures, particularly as regards the r $\{101\}$ faces, but in general the relationships are clearly linear.

It may be said, therefore, that the rates of growth of the faces are given by

$$\frac{dG}{dt} = K(C - Co).$$

where G = growth of the face in a normal direction

C = Concentration of solution in contact with the face (i.e. the concentration of the bulk of the solution if this is flowing past the crystal at relatively infinite velocity).

C_o = Saturation concentration

K = the velocity constant for the face, which is dependent on temperature.

TABLE II.

25°C

Saturation concentration = 67.36 gms/100 gms. solution; Co = 84.96 gms/100 ccs.

Solution				Maximum Rates of Growth of Faces (mms./hour)									
				a		p		p^1		o		r^1	
Conc. % wt.	S/satn. C-Co	S/satn Coeff.		100	$\bar{1}00$	110	$\bar{1}10$	$1\bar{1}0$	$\bar{1}\bar{1}0$	001	$00\bar{1}$	$10\bar{1}$	$\bar{1}0\bar{1}$
69.32	3.50	1.095		.0090	.0080	.0292	.0268	.0120	.0110	.0111	.0090	.0165	.0145
			Mean	.0085		.0280		.0115		.0101		.0155	
70.96	6.45	1.184		.0180	.0170	.0483	.0457	.0187	.0173	.0197	.0184	.0329	.0313
			Mean	.0175		.0470		.0180		.0191		.0321	
71.83	8.00	1,236		.0220	.0180	.0623	.0661	.0233	.0217	.0222	.0260	.0394	.0372
			Mean	.0200		.0642		.0225		.0241		.0383	
73.75	11.41	1.361		.0300	.0279	.092	.078	.0371	.0330	.0334	.0293	.0510	.0551
			Mean	.0290		.085		.0351		.0314		.0531	

TABLE 12

30°C

Saturation concentration = 68.27 gms/100 gms solution; Co =   gms/100 ccs.

Solution				Maximum Rates of Growth of Faces (mms/hour)										Overall velocity of crystallisation mgms/m^2/min.
Conc. % Wt.	S/satn. C-Co	S/satn Coeff.		a		p		p^1		c		r^1		
				100	$\bar{1}00$	110	$\bar{1}\bar{1}0$	$\bar{1}10$	$1\bar{1}0$	001	$00\bar{1}$	$10\bar{1}$	$\bar{1}01$	
70.12	3.25	1.091		.014	.012	.045	.041	.020	.018	.019	.014	.028	.023	-
			Mean	.013		.043		.019		.017		.026		
71.03	4.88	1.140		.020	.022	.067	.072	.029	.032	.027	.030	.038	.036	940
			Mean	.021		.070		.031		.029		.037		
71.71	6.11	1.178		.026	.026	.084	.085	.030	.028	.027	.031	.040	.040	-
			Mean	.026		.085		.029		.029		.040		
73.02	8.47	1.258		.040	.036	.119	.125	.044	.046	.044	.042	.059	.057	1630
			Mean	.038		.122		.045		.043		.058		
73.50	9.31	1.289		.041	.042	.127	.131	.045	.048	.045	.047	.066	.065	1900
			Mean	.042		.129		.047		.046		.066		
75.08	12.30	1.300		.055	.050	.176	.180	.070	.064	.072	.065	.086	.098	3170
			Mean	.053		.178		.067		.069		.092		

TABLE 13.

40°C

Saturation concentration = 70.17 gms/100 gms solution; Co = 93.84 gms/100 ccs.

Solution				Maximum Rates of Growth of Faces (mms/hour)						Overall velocity of crystallisation mgms/m^2/min.
Conc. % Wt.	S/satn. C-Co	S/satn Coeff.		a 100 $\bar{1}00$	p 110 $\bar{1}10$	p^1 $1\bar{1}0$ $\bar{1}\bar{1}0$	c 001 $00\bar{1}$	r^1 $10\bar{1}$ $\bar{1}01$	r 101 $\bar{1}0\bar{1}$	
71.86	3.02	1.086	Mean	.033 .035 .034	.130 .129 .130	.055 .049 .052	.045 .050 .048	.073 .067 .070	.068 .060 .064	1200
72.85	4.83	1.141	Mean	.049 .051 .050	.184 - .184	.067 - .067	.063 .061 .062	.089 .087 .088	.085 .075 .080	2250
74.02	6.95	1.211	Mean	.073 .072 .073	.292 .284 .288	- .107 .107	.099 .104 .102	.140 .124 .132	.111 .152 .132	3900
75.13	8.97	1.284	Mean	.102 .103 .103	.346 .364 .355	.155 .154 .155	.133 .134 .134	.190 .185 .188	.192 .195 .194	4900
76.23	11.01	1.363	Mean	.122 .132 .127	.446 .406 .426	.160 .166 .163	.172 .160 .166	.205 .218 .212	- - -	6770

TABLE 14.

50°C.

Saturation concentration = 72.19 gms/100 gms solution; Co = 97.03 gms/100 ccs.

Solution				Maximum Rates of Growth of Faces (mms/hour)												Overall velocity of crystallisation mgms/m^2/min
Conc. % Wt.	S/Satn. C-Co	S/satn Coeff.		a		p		p^I		c		r^I		r		
				100	$\bar{1}00$	110	$\bar{1}10$	$1\bar{1}0$	$\bar{1}\bar{1}0$	001	$00\bar{1}$	$10\bar{1}$	$\bar{1}01$	101	$\bar{1}0\bar{1}$	
73.28	1.95	1.057		.044	.045	.148	.138	.057	.051	.048	.052	.069	.070	.064	.076	1400
			Mean	.045		.143		.054		.051		.070		.070		
73.87	3.06	1.089		.066	.062	.297	.296	.090	.082	.081	.071	.120	.120	.128	-	3000
			Mean	.064		.297		.086		.076		.120		.128		
74.35	3.96	1.117		.083	.085	.250	.280	.100	.093	.104	.096	.149	.151	.160	.120	3100
			Mean	.084		.265		.097		.100		.150		.140		
75.30	5.67	1.174		.122	.124	.395	.365	.125	.155	.133	.130	.192	.195	.200	.187	5200
			Mean	.123		.380		.140		.132		.194		.194		
75.52	6.07	1.188		.136	.139	.423	.445	.159	.149	.165	.149	.230	.239	-	-	6020
			Mean	.138		.436		.154		.157		.235				

TABLE 15.

60°C.

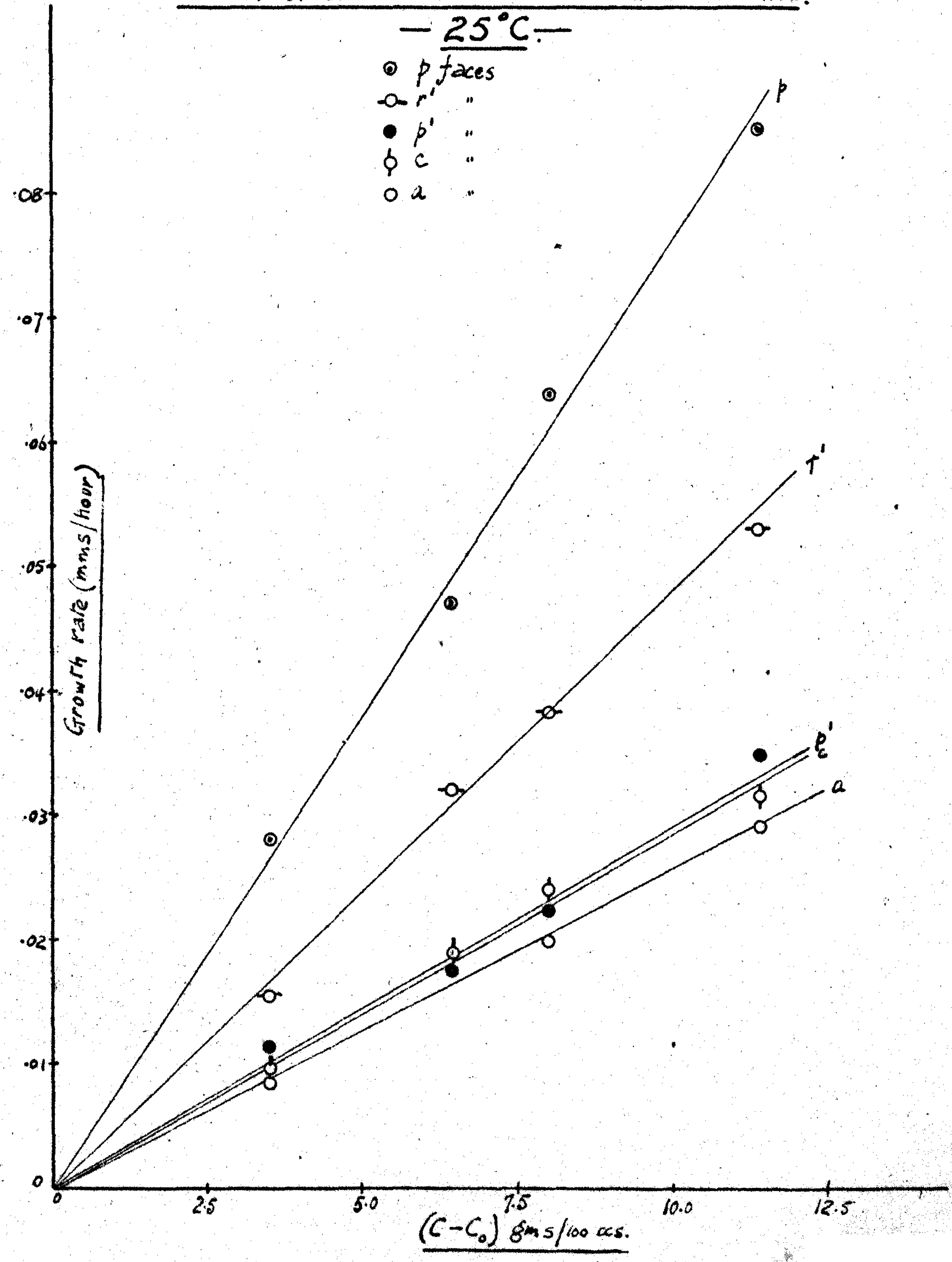
Saturation concentration = 74.32 gms/100 gms solution ; Co = 100.44 gms/100 ccs.

Solution				Maximum Rates of Growth of Faces (mms/hour)						Overall Velocity of Crystallisation mgms/m^2/min.
Conc. % Wt.	S/satn. C-Co	S/satn Coeff.		a 100 $\bar{1}00$	p 110 $\bar{1}10$	p^1 $1\bar{1}0$ $\bar{1}\bar{1}0$	c 001 $00\bar{1}$	r^1 $10\bar{1}$ $\bar{1}01$	r 101 $\bar{1}0\bar{1}$	
75.38	1.96	1.058	Mean	.054 .070 .062	.203 .189 .196	.082 .088 .085	.081 .089 .085	.128 .116 .122	.140 .124 .132	2700
75.67	2.50	1.075	Mean	.087 .083 .085	.270 .290 .280	.090 .109 .100	.118 .101 .110	.163 .177 .170	.160 .122 .141	3300
76.16	3.39	1.104	Mean	.120 .110 .115	.350 .332 .341	.155 .154 .153	.138 .132 .135	.220 .202 .211	.200 .170 .185	4100
76.72	4.44	1.139	Mean	.121 .137 .129	.529 .503 .516	.182 .200 .191	.190 .174 .182	.280 .296 .288	.358 .288 .320	7370
77.07	5.08	1.161	Mean	.158 .154 .156	.536 .564 .550	.209 .201 .205	.197 .238 .218	.343 .281 .312	.310 .360 .335	7700

— FIGURE 25 —

EFFECT OF SUPERSATURATION ON GROWTH RATE.

— 25°C. —



— FIGURE 26 —

EFFECT OF SUPERSATURATION ON GROWTH RATE.

— 30 °C. —

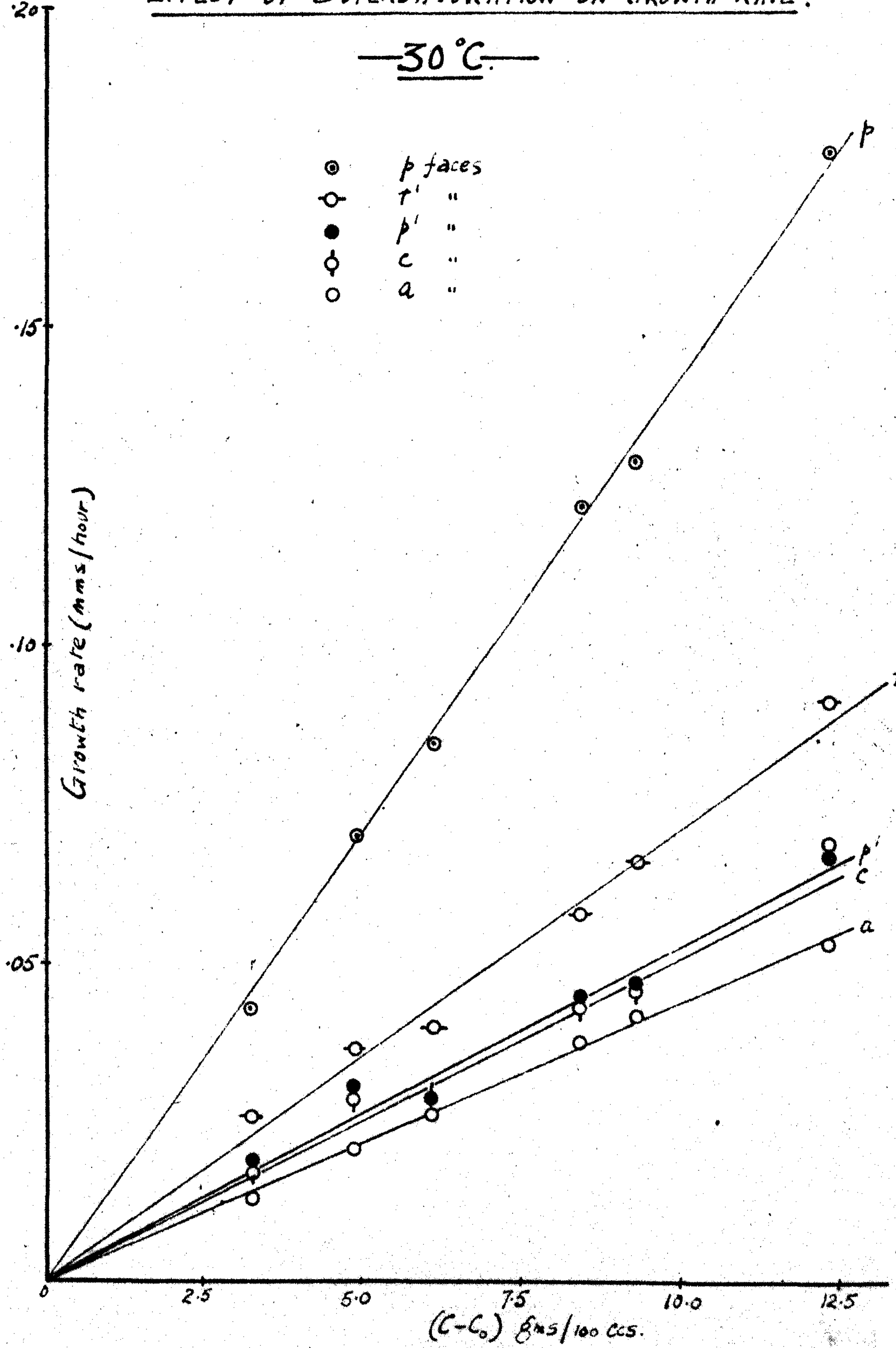
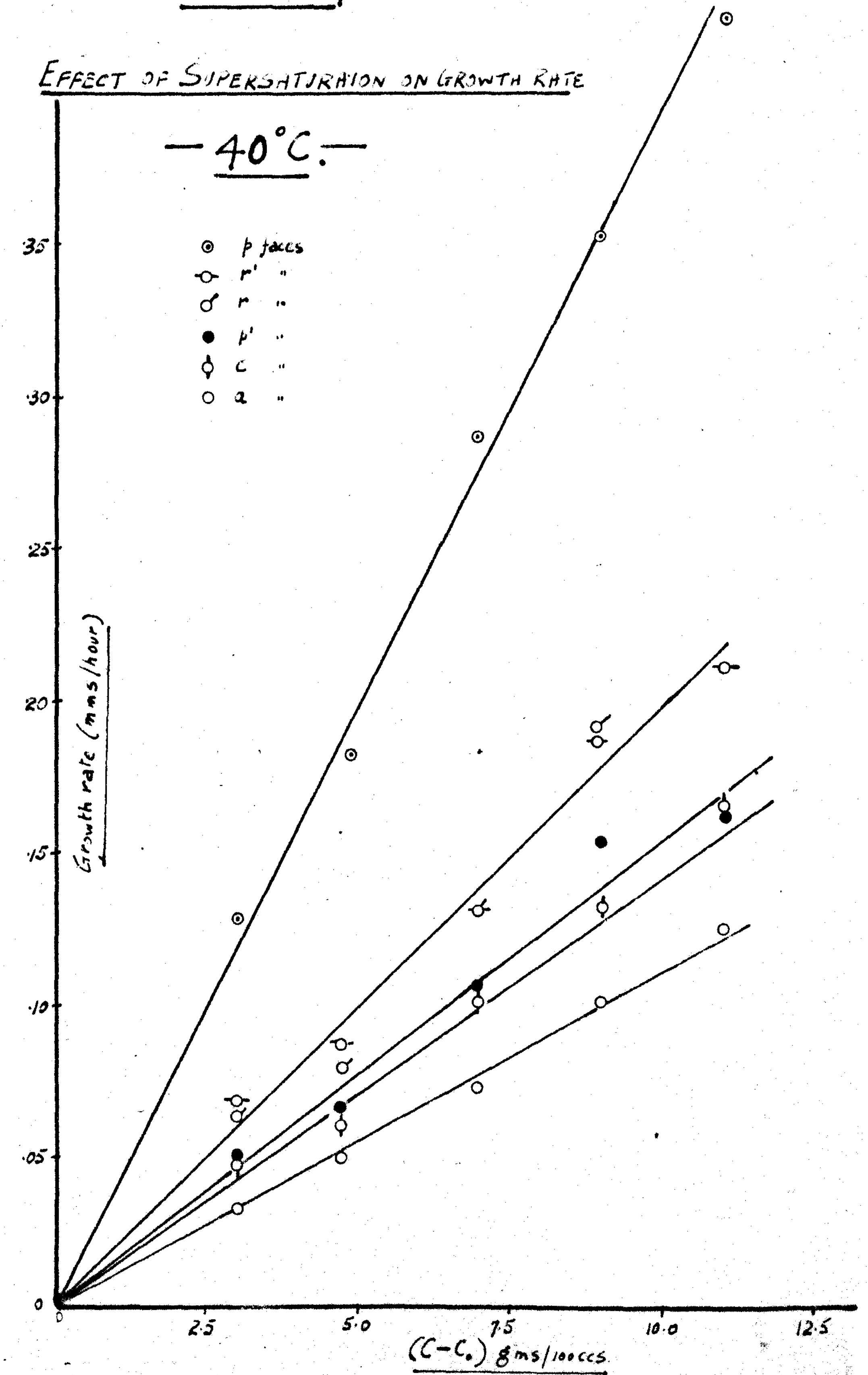
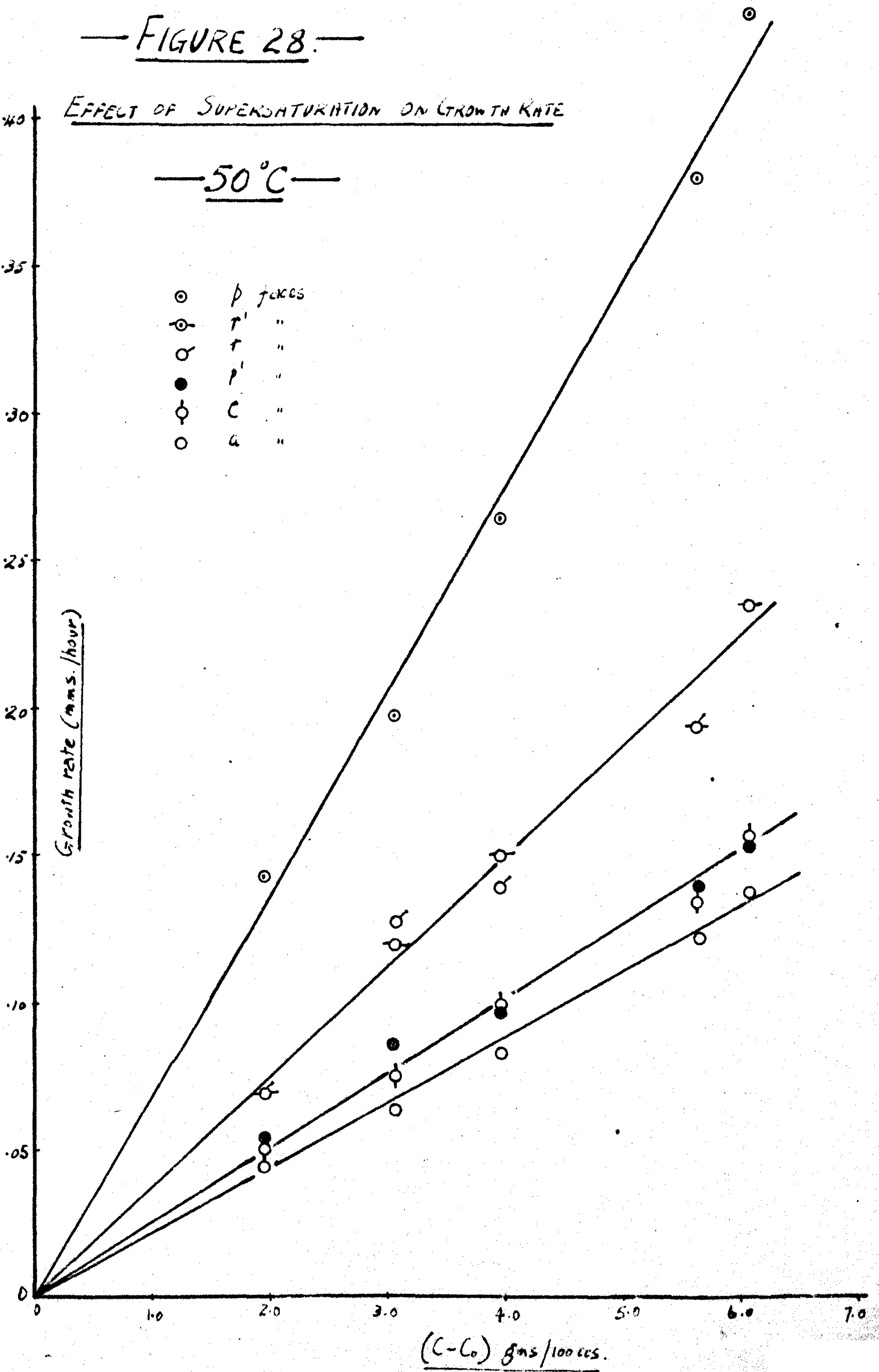


FIGURE 27

EFFECT OF SUPERSATURATION ON GROWTH RATE



—FIGURE 28.—



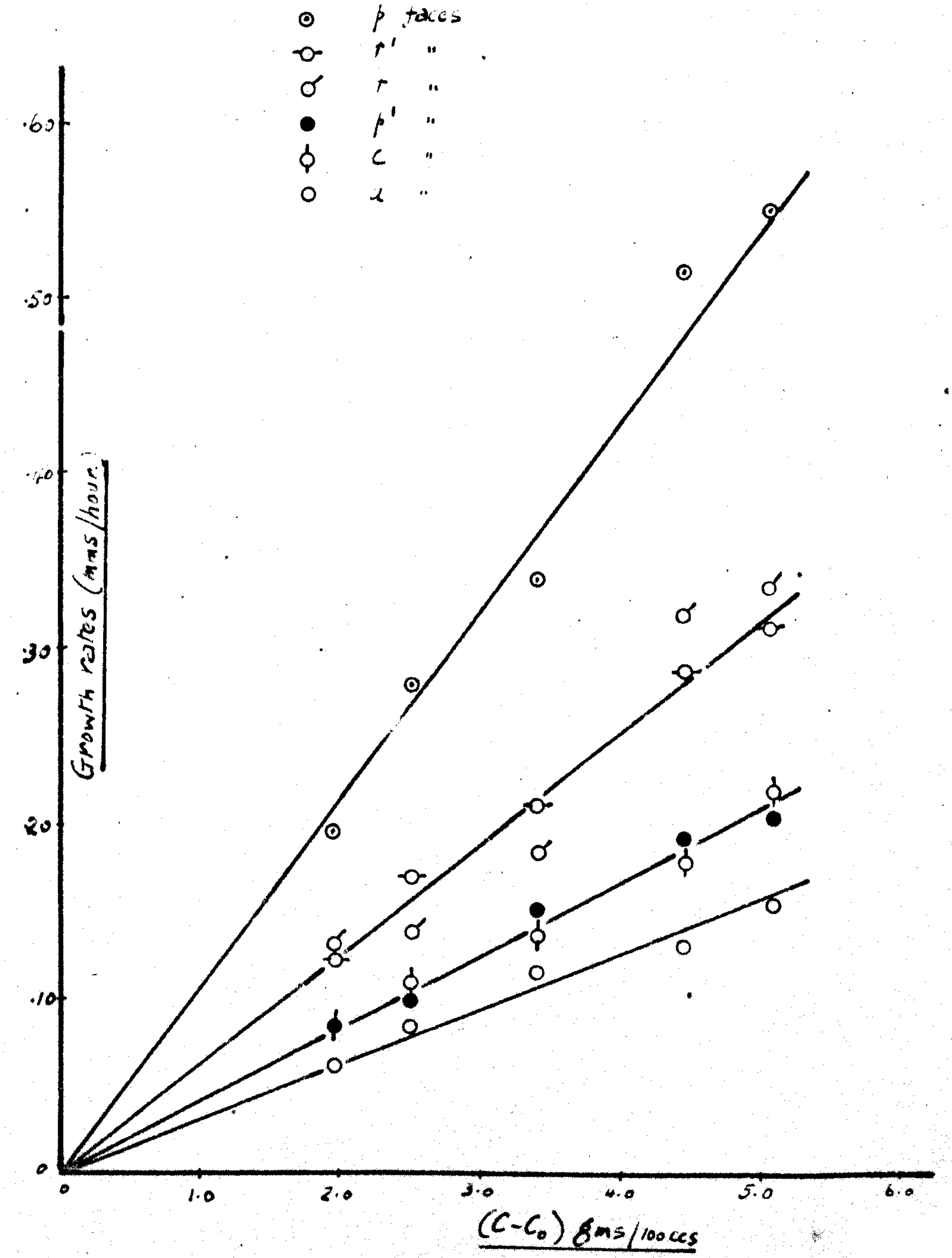
EFFECT OF SUPERSATURATION ON GROWTH RATE

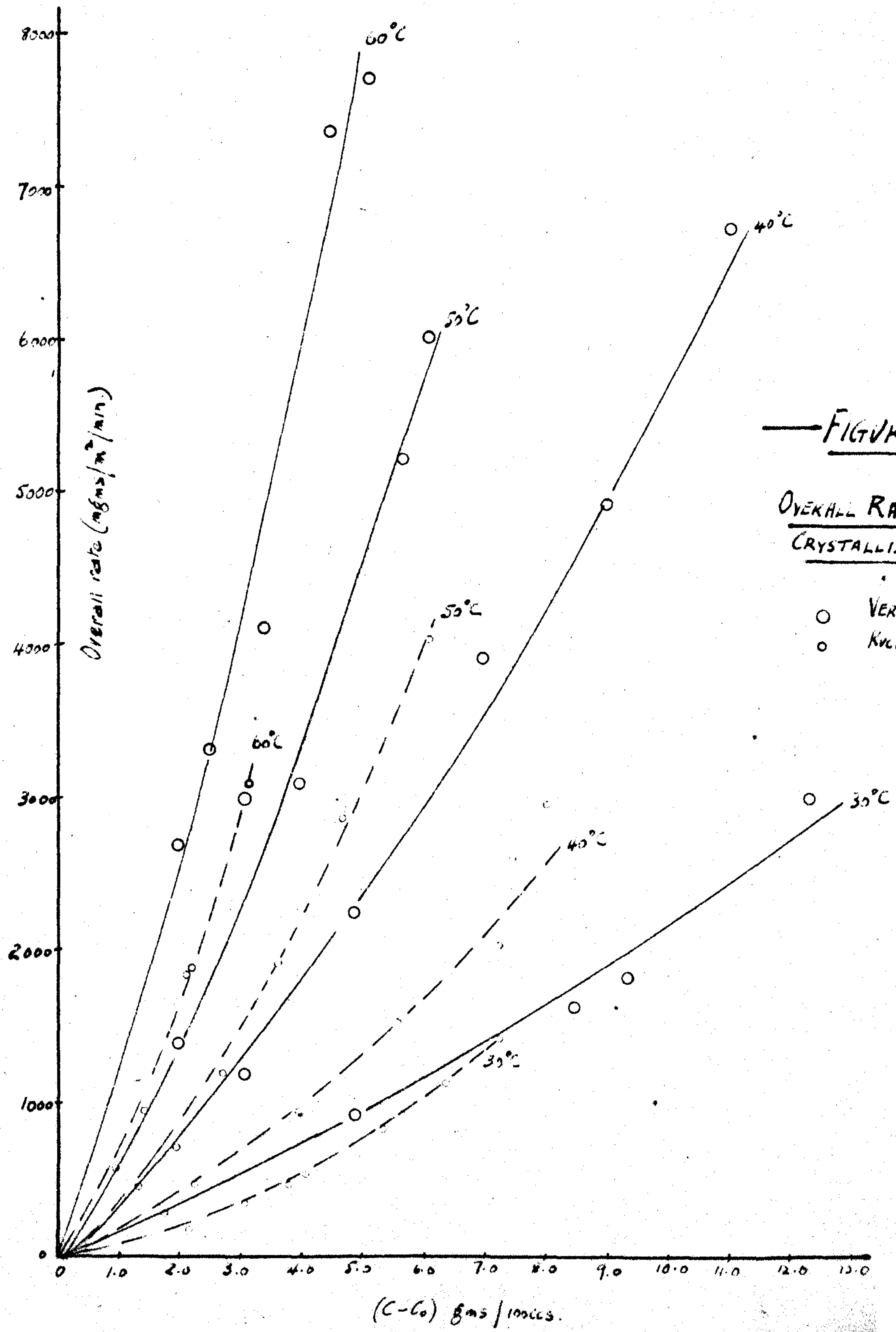
—50°C—

—FIGURE 29—

EFFECT OF SUPERSATURATION ON GROWTH RATE

—60°C—





—FIGURE 30—

OVERALL RATES OF CRYSTALLISATION

The values of K for each pair of faces, obtained from the lines of best fit on the graphs are given below in Table 16, growth rates being in mms/hour and supersaturations in gms/100 ccs solution. If growth is expressed as gms sucrose crystallised /sq. cm/sec, and the supersaturations in gms/cc, the K values given in Table 16 should be multiplied by 4.396×10^{-3}.

TABLE 16.

Velocity Constants of Faces.

Faces.	Values of K = $\frac{dG/dt}{C-C_o}$				
	25°	30°	40°	50°	60°
a 100 $\bar{1}00$	.00255	.00440	.0112	.0222	.0320
c 001 $00\bar{1}$	.00285	.00507	.0141	.0256	.0410
p^1 $1\bar{1}0$ $\bar{1}\bar{1}0$	.00290	.00525	.0155	.0256	.0420
r 101 $\bar{1}0\bar{1}$	-	-	.0200	.0374	.0635
r^1 $10\bar{1}$ $\bar{1}01$	.00480	.00705	.0200	.0374	.0635
p 110 $\bar{1}10$	.00763	.0143	.0397	.0695	.1080

The accuracy of the measurements of the $r\ \{101\}$ faces was not as high as with the other faces, and the points for this form on the graphs are rather scattered. The growth rates seem however, to be approximately equal to those of the $r^1\{10\bar{1}\}$ faces, and in the table given above, the same velocity constants have been assigned.

Discussion of Results.

It will be seen that marked differences occur in the growth rates of the various crystal faces. Minimum rates are shown throughout by the $a\{100\}$ faces while $p\ \{110\}$ faces grow with the highest velocity. The growth rates of the $p^1\ \{1\bar{1}0\}$ and $p\ \{110\}$ faces, at the left and right poles of the crystal respectively are considerably different.

Unfortunately, very little is known at present of the structure of the sucrose crystal. The sugars in general present one of the most difficult problems to be attacked by the methods of X-ray crystallography. The shapes of the molecules depart very much from the planar and linear varieties which have been so successfully dealt with, and little or no help may be obtained from optical data. The most that can be said at present on the subject is that "the hardness, high melting point, and high density of the sugar suggest that the X-ray structure is largely determined by the O H groups, which tend to interact to the greatest possible extent and link the molecules together in all directions." (37)

The one cleavage plane of the sucrose crystal is the (100). The cleavage indicates that intermolecular forces are least in directions normal to this plane, and the low growth rates of the 100 faces confirm this.

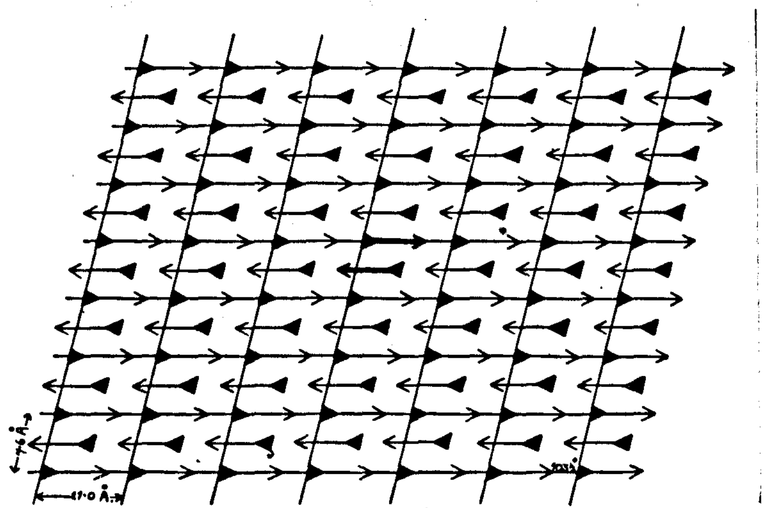
The unit cell dimensions of sucrose have been determined (38) and are as follows:

a = 11.0 Å
b = 8.7 Å
c = 7.6 Å

There are two molecules in the unit cell.

According to Astbury (39) the molecules are arranged as in Figure 31, in the ac plane of the crystal. An alternative "head and tail" arrangement is indicated.

An examination of a molecular model of sucrose will show the complexity of the arrangement of the atoms. Attempts were made to arrive at some explanation of the specific differences in the growth rates of the faces that have been observed by altering the relative positions of the



— FIGURE 31 —

constituent groups as much as was possible, but without success. It must be however, that there is some difference in distribution of say the O H groups in the molecule, and that some polar effect is exerted.

The effect of temperature on crystallisation rate is marked, as can be seen from the tables and graphs. According to the general theory of activation applied to reaction, velocity in solution, the rate at which molecules undergo reaction is proportional to the number of molecules in an appropriately activated condition. This number in turn is an exponential function of the temperature and of the energy of activation, and usually determines the magnitude of the reaction velocity.

The equation

$$K = Ze^{-\frac{E}{RT}} \qquad \text{----} \ (1)$$

(Where K = velocity constant, R = gas constant, T = absolute temperature, and E and Z are specific constants), has been found to apply to the great majority of reactions both homogeneous and heterogeneous.

Taking logs of equation (1)

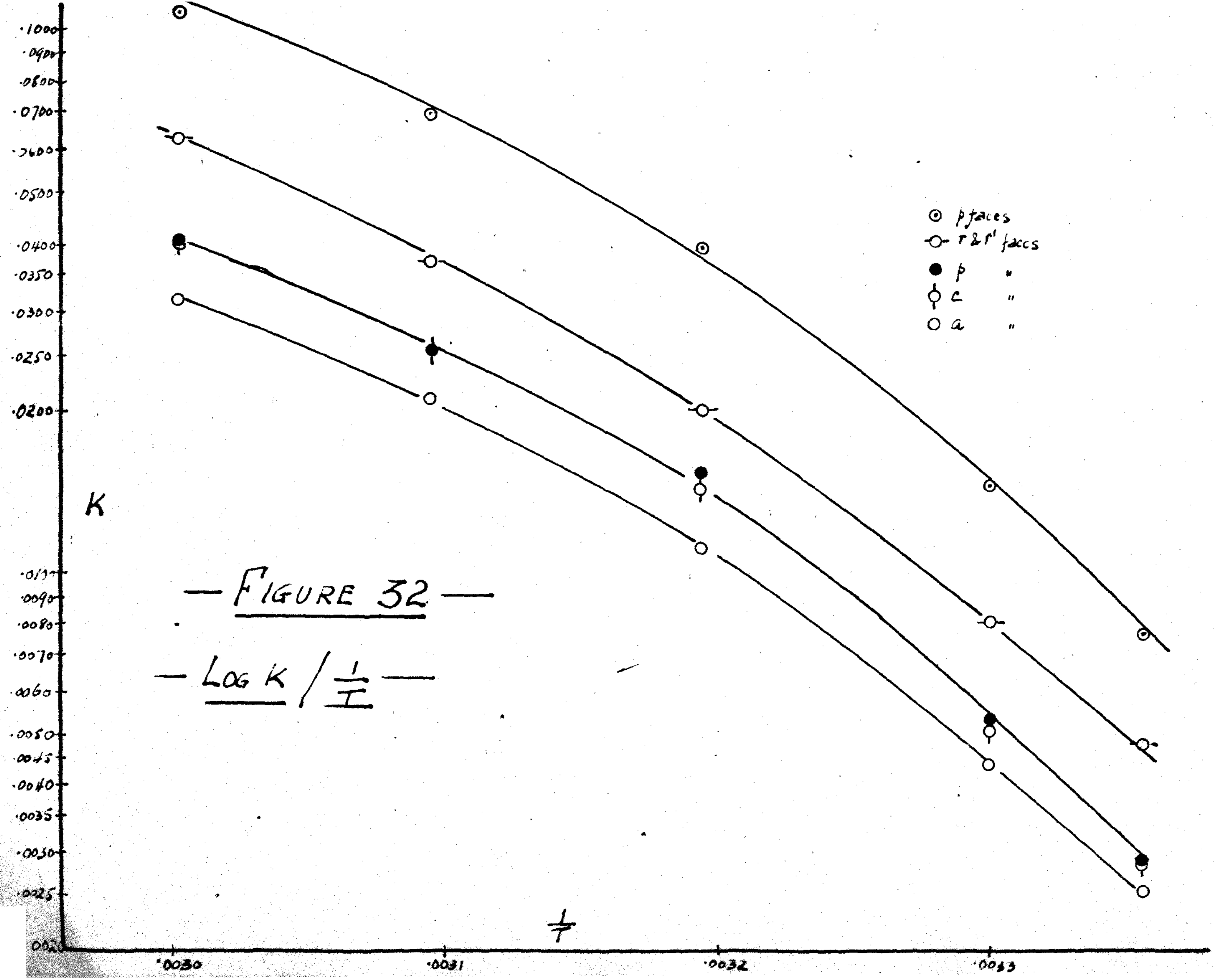
$$\log_e K = \log_e Z - \frac{E}{RT} \qquad \text{----} \ (2)$$

i.e. the logarthm of the velocity constant plotted against the reciprocal of the absolute temperature should give a straight line, the slope of which is $-\frac{E}{R}$.

The velocity constants of Table 16 have been plotted in this manner in the graph Figure 32. It will be seen that the curves depart somewhat from linearity. Within experimental error, the curves for the various faces are parallel to one another.

In view of the non-linear relationship, it would seem that the concepts of activation usually applied to reaction velocity in solution need some modification in the case of the crystallisation of sucrose. The concentrations of the solutions involved are so high that this would perhaps be expected.

As regards Kucharenko's results, which are shown graphically in Figure 30, it will be seen that in all cases the velocities of crystallisation determined by the writer are higher. At 30°C. the divergence is least. The reason for these differences will be clear from the discussion given in Section IV of the effect of rate of flow of solution on crystallisation velocity. The conditions of Kucharenko's determinations, where crystals were placed in rotating bottles of solution, were such that maximum crystallisation rates were not reached, the effect being more marked at higher velocities. At 30°C the velocities are fairly small, and rotation in a bottle would give results not far from the maximum.



— FIGURE 32 —

— LOG K / $\frac{1}{T}$ —

VI GENERAL DISCUSSION.

It is doubtful whether the method that has been developed for the present work would be generally applicable to the study of crystallisation from solution. The factor which is of importance in the use of the method is the rate of spontaneous crystallisation. With many inorganic substances this is high, and the possibility of crystallisation taking place in the cooling coils and on the walls of the cells would be considerable. Sucrose presents many advantages in this respect although the use of such highly viscous solutions introduces other experimental difficulties. It seems possible, however, that the method could be modified so as to make it suitable for use with some other substances.

Some of the results obtained with sucrose such as those dealing with the differing velocity constants of the faces, and the effect of temperature on the process, are at present practically impossible to interpret on account of the lack of knowledge of the crystalline structure, and the constitution of concentrated solutions. These points would be more advantageously investigated with simpler substances whose crystal structures are fully known.

Sucrose, however, has proved a convenient substance for the investigation of the effect of rate of flow of solution on crystallisation rate, and it is thought that as regards this point fairly definite conclusions may be drawn. The Nernst hypothesis, of a saturated layer of solution in contact with the crystal was seen to be inapplicable in the case of sucrose, the slow rate of crystallisation making this very evident. For the process of crystallisation from solution in general there appears to be no necessity to introduce the concept, since it would seem that the solution in the immediate vicinity of the crystal face will have a concentration dependent on three factors

1) The velocity constant of the crystal face
2) The diffusion coefficient of the substance
3) The rate of flow of solution relative to the face.

For any set of conditions, the concentration of solution on the face should reach a definite value. The lower the velocity constant, and the higher the rate of flow, the more nearly will the concentration on the face approach that of the bulk of the solution. In some reactions which have previously been studied, particularly those of dissolution, the velocity constant appears to be high and unless the rate of flow of solution is correspondingly increased, the concentration of solution on the face would take on a value not far from the saturation concentration. It seems very probable, however, that with sufficiently high rates of flow, the concentration on the face could always be made to approximate to that of the bulk of the solution.

It is notable that despite the amount of work that has been published to date on velocity of crystallisation from solution there are no accepted absolute values for the velocity constants of these reactions, the greater proportion of the published results having only empirical significance. One of the main reasons for this would seem to be the failure to account for or eliminate the effect of rate of flow of solution on the process, Kucharenko's results for sucrose exemplifying this point.

It was shown in the present work that if the effect of rate of flow of solution is eliminated, the reaction is monomolecular in all cases, i.e., the reaction velocity is proportional to the supersaturation, $C - C_0$, of the solution, a result which is perhaps reasonable to expect, and which might well prove to be applicable to crystallisation in general.

PART 2.

THE SOLUBILITY OF SUCROSE IN PURE SOLUTION.

The solubility figures of Herzfeld (26) have been accepted as practically standard for many years, despite the fact that from time to time determinations at a few temperatures have been reported, which have not always been in good agreement. In particular, Grut (40) in a recently published paper found quite wide discrepancies.

In view of the importance of an accurate knowledge of the solubility of sucrose at various temperatures for the work on velocity of crystallisation, a redetermination was made.

For the case of sucrose, the standard solubility technique (stirring with excess solute at constant temperature until equilibrium is reached) has a number of disadvantages.

1) Equilibrium is reached very slowly, necessitating stirring for long periods.
2) At higher temperatures appreciable inversion and decomposition take place if the experiment is protracted.
3) The separation of the excess sucrose from the saturated solution without evaporation taking place, is not an easy matter with the highly viscous solutions encountered.

The second point mentioned above has been found (41) to be of major importance when investigating solubility at higher temperatures in impure sucrose solutions containing reducing sugars, where the rate of decomposition is such that equilibrium cannot be attained.

A modification of the usual solubility technique seemed therefore to be desirable. It was suggested to the writer by Dr. R. W. Harman that a method involving the determination of the saturation temperature of a given solution, instead of the saturation concentration at a given temperature would be advantageous. A rapid industrial method based on this principle has been developed by Harman (42), who used a flat-sided glass cell, through which water of known temperature could be pumped, mounted on the stage of microscope.

A thin film of supersaturated solution containing minute crystals is placed under a cover glass on top of the cell and the temperature raised until dissolution of crystal edges is observed. Empirical corrections are necessary on account of the temperature lag involved in the heating. To obtain a method suitable for absolute determinations, the following apparatus was adopted.

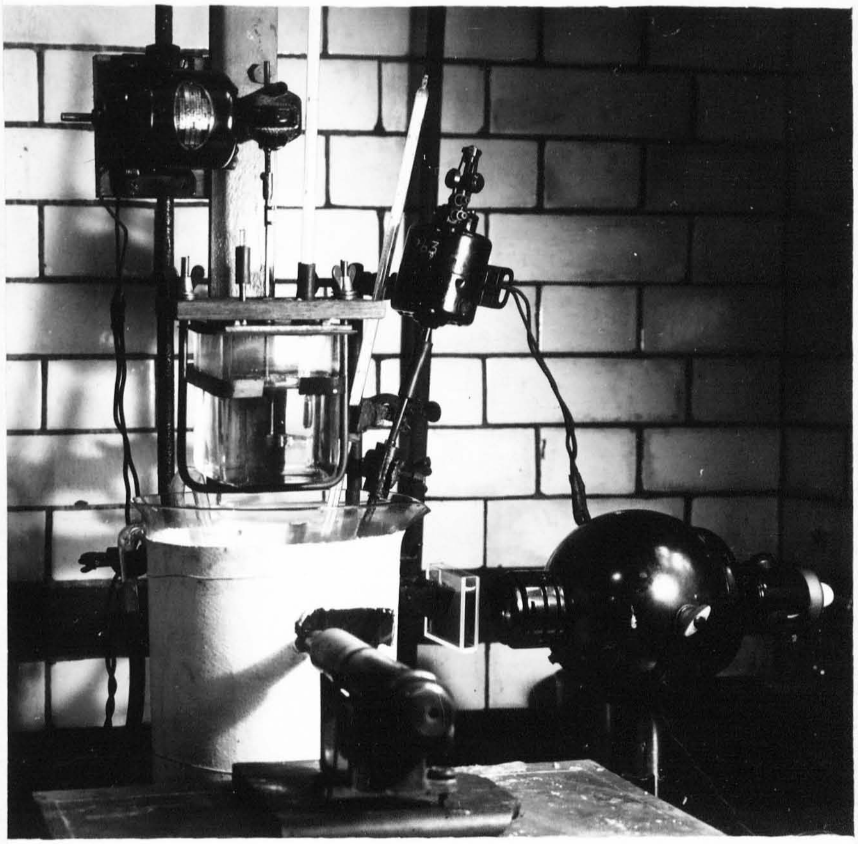
Experimental Method.

It was remarked previously that supersaturated solutions of sucrose do not show a marked tendency towards rapid spontaneous crystallisation, and use was made of this fact in developing the method.

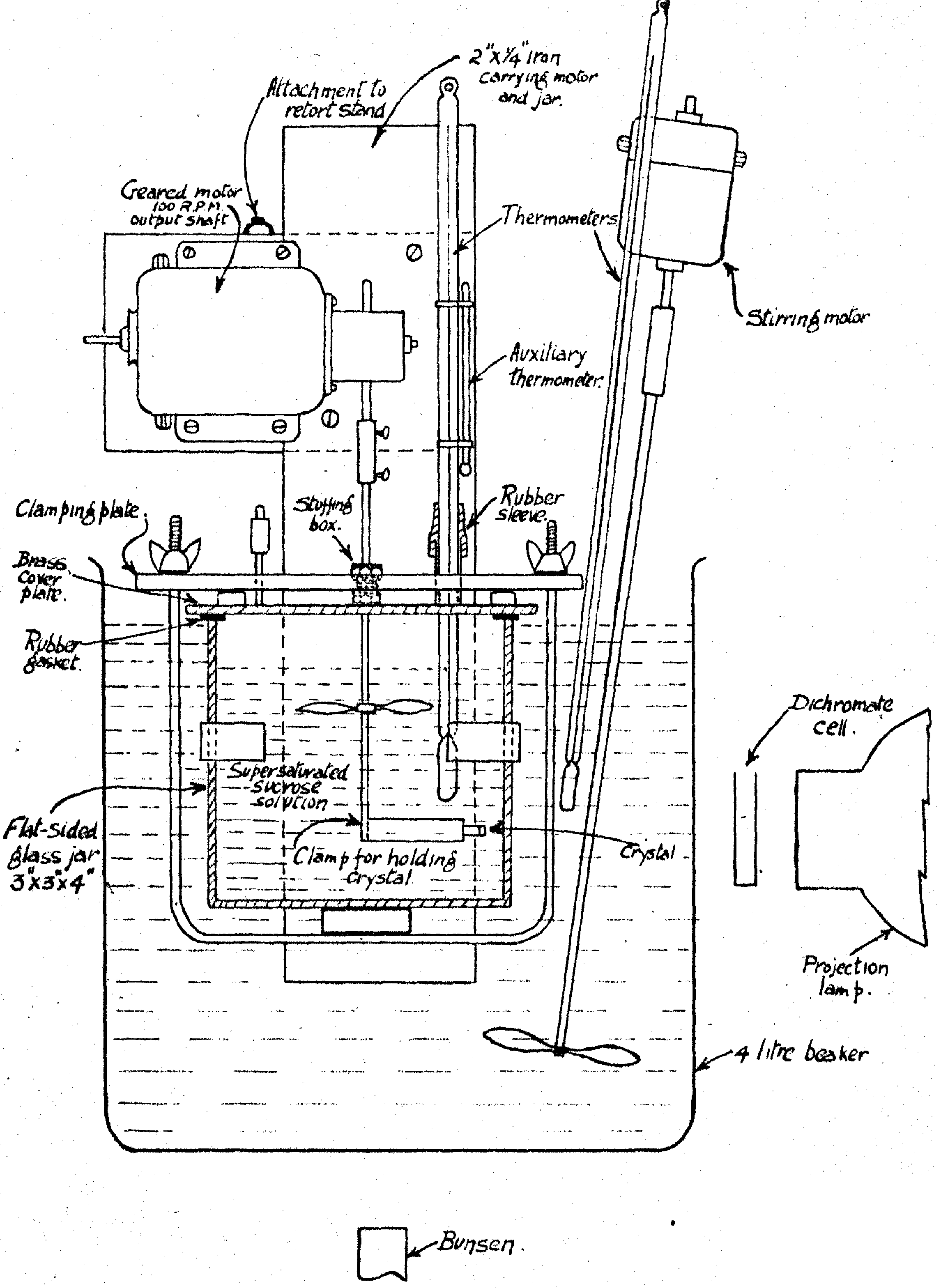
Essentially the method consists in rotating a crystal in a glass vessel containing about 400 ccs. of slightly supersaturated solution, raising the temperature of the latter in steps of 0°2 C. and holding at each temperature for five to ten minutes. The crystal is illuminated from the side, and viewed through the front of the vessel with a low power microscope. When erosion of the crystal is observed, the solution is sampled and analysed.

A photograph, Figure 33, gives a general view of the arrangement, the vessel containing the solution being raised to show its construction, while the diagram Figure 34 shows the details of the apparatus as seen from the front.

A flat sided glass jar, 3" square x 4" high with flat ground top edges, was fitted with a rubber gasket and brass cover plate. The latter was drilled centrally and a small stuffing box attached to carry a 3/32" brass spindle. A nickel plated clamp was attached at right angles to the end of the spindle, to hold a small crystal, and the projecting



— Figure 33 —



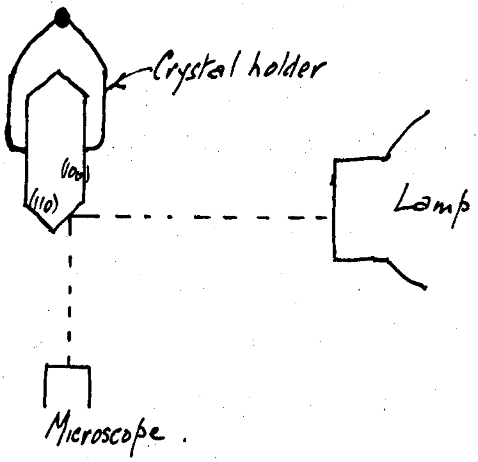
— FIGURE 34 —

— SOLUBILITY APPARATUS —

end connected to a 1/16 H.P. motor with built-in gearing, which ran at about 100 R.P.M. on the output shaft. The jar and motor were both attached to a short length of 2" x 1/4" iron as can be seen from the photograph, and this connected to a heavy retort stand so that jar and motor could be raised or lowered as one unit.

The brass cover to the jar was fitted with a short length of ~~thin~~ pipe through which passed a thermometer graduated to 0°.1 C. A rubber sleeve served to make this connection airtight. In addition a short length of pipe was attached to the cover to allow pressure to be applied to the jar when necessary. The cover was held firmly to the jar by means of a clamping plate and brass rod bent as shown and threaded to take wing nuts. The assembly was perfectly airtight. The glass jar was surrounded by a 4-litre beaker filled with water and heated by a bunsen, stirrer and thermometer being inserted in the beaker.

The method of observation was to fix a small crystal freshly grown from solution, in the clamp, illuminate from the right hand side with a projection lamp, and observe through the front with the microscope shown in the photograph Figure 33. The following sketch shows the plan view of crystal, lamp, and microscope:



The crystal is held by the $\{100\}$ faces in the clamp, and the lamp and microscope adjusted so that a good reflection is obtained from one of the $\{110\}$ prism faces, the other prism face being not illuminated. The dividing line, the end prism edge, is very sharp and distinct in a good crystal. If any erosion occurs, the edge becomes slightly blurred and irregular, and it has been found that erosion can be very readily detected in this manner. A cell containing a weak solution of potassium dichromate is placed in front of the lamp as the yellow light appears to improve the ease of observation.

In carrying out a determination the solution is prepared by making an approximately 50% solution of pure sucrose filtering with a little washed kieselguhr, and evaporating at about 30-35°C. to the required concentration. High supersaturations may safely be reached with the very pure solutions used. A refractive ~~under~~ index determination is made, and the approximate concentration and saturation temperature calculated.

Having inserted a crystal in the clamp, the glass vessel of the apparatus is closed, lowered into the beaker, and the temperature of the water raised to within about 1°C. of the calculated saturation temperature of the solution. After heating the solution to the same temperature it is run into the vessel through the thermometer opening, the thermometer inserted, and the motor started.

After rotating for 5 to 10 minutes the motor is stopped and the crystal swung round into the field of the microscope for observation. After adjusting the lamp to obtain a reflection from one of the $\{110\}$ faces, it can be seen whether dissolution has taken place. If this is not so, the temperature is raised 0°2 C, and the crystal rotated for a further period.

Temperature is readily controlled by hand as the sucrose solution only responds slowly to changes in the temperature of the water bath.

The point will finally be reached when slight erosion of the end edge of the crystal is observed. The saturation temperature of the solution is taken to be the mean of the temperatures before and after dissolution. Correction is applied when necessary for emergent thermometer stem, a small auxiliary thermometer being attached for this purpose. All thermometers were carefully checked against N.P.L. standards.

At the dissolution point, the thermometer is withdrawn, and a dry glass tube of the same external diameter, bent into the shape of an inverted U, inserted, the end dipping below the surface of the solution. Applying slight pressure to the vessel through the other opening in the cover plate, approximately the required amount of solution is forced over into a tared 100 cc. flask, the flask stoppered, cooled and weighed, and the sucrose determined polarimetrically as described previously, p.24. Duplicate or triplicate analyses were done in each case. Another sample of the solution was analysed for reducing sugar content.

Working in this manner, a saturation temperature may be determined within half an hour. The final solution analysed was in all cases free of crystals. At the higher temperatures, the glass vessel was lowered so that the brass cover plate was beneath the surface of the water, as it was found that condensation of water took place on the cold surface if this was not done.

The highly pure commercial sucrose used for the velocity of crystallisation work was employed. The time taken for an experiment was so short that no appreciable amount of reducing sugars was formed, the reducing sugar content of the final solutions being in all cases less than 0.01%. Errors due to this cause, either as regards the effect on the polarimetric determination or on the solubility of sucrose are negligible.

Results.

Fourteen solutions were investigated, over the range 17.6 to 91.1°C. The results are shown below in Table 17, concentrations being expressed in gms per 100 gms solution. Plotting concentration against temperature as in Figure 35 (heavy line) a parabola is obtained, the curve of best fit, found by the method of least squares being a quadratic parabola

$$C = 63.256 + 0.1497\,t + 0.000578\,t^2$$

where C = concentration in gms/100 gms solution

t = temperature °C.

Concentrations calculated by this formula are shown in the second column of the table.

FIGURE 35

SOLUBILITY OF SUCROSE

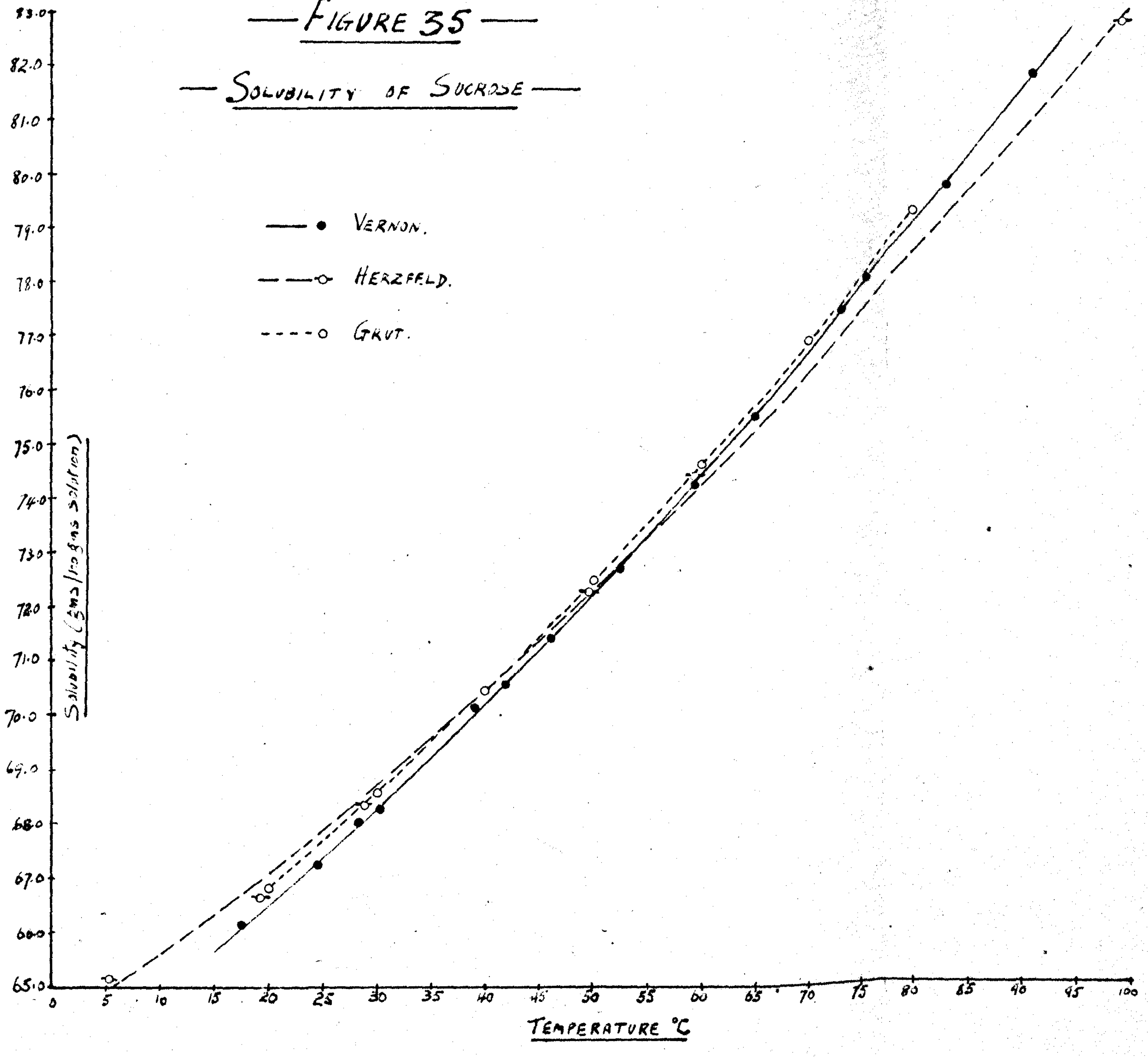


TABLE 17.

Solubility of Sucrose in Pure Solution.

Temp. °C.	Concentration in gms/100 gms solution	
	Observed	Calculated.
17.6	66.13	66.07
24.7	67.24	67.31
28.4	68.00	67.97
30.4	68.26	68.34
39.1	70.11	69.99
42.0	70.52	70.56
46.1	71.39	71.39
52.6	72.66	72.73
59.5	74.20	74.21
65.0	75.45	75.43
73.2	77.39	77.31
75.6	77.92	77.88
83.2	79.63	79.71
91.1	81.71	81.69

If the temperatures are assumed to be free of error, the probable error of the concentration determinations as calculated from the fit of the curve is ± 0.04. Actually temperatures are also subject to experimental error, probably about ± 0°.1 C, and the concentrations would be about ± 0.03

Comparison with Results of Herzfeld and Grut.

Table 18 shows the solubility figures of Herzfeld (26), Grut (40) and the writer at intervals of 5°C, the equation given above being used to calculate the latter values. The equation has been used to extrapolate over a small interval at both ends of the scale (i.e. to 15° and 95°C).

Referring first to Herzfeld's work, the solubility was determined at six temperatures, ranging from 5°.2 to 99°.45C, no determination being made between 59°.4 and 99°.45 C. An equation was derived by the least squares method,

$$C = 64.184 + 0.1348\ t + 0.000531\ t^2.$$

In Table 19 following, the experimental and calculated values are shown. The results are plotted in the graph Figure 36.

TABLE 18.

Solubility of Sucrose

Temperature.	Concentration (gms/100 gms solution).		
	Herzfeld	Grut	Vernon
15	66.33	-	65.63
20	67.09	66.80	66.48
25	67.89	67.68	67.36
30	68.70	68.58	68.27
35	69.55	69.50	69.20
40	70.42	70.45	70.17
45	71.32	71.43	71.16
50	72.25	72.43	72.19
55	73.20	73.46	73.24
60	74.18	74.53	74.32
65	75.18	75.64	75.43
70	76.22	76.78	76.57
75	77.27	77.95	77.74
80	78.36	79.15	78.93
85	79.46	-	80.16
90	80.61	-	81.45
95	81.77	-	82.69
100	82.97	-	-

TABLE 19.

Solubility of Sucrose (Herzfeld)

Temp. °C.	Concentration (gms/100 gms solution)		
	Observed	Calculated	Difference
5.20	65.17	64.90	- 0.27
19.15	66.65	66.95	0.30
28.80	68.31	68.50	0.19
49.53	72.23	72.16	- 0.07
59.40	74.33	74.06	- 0.27
99.45	82.76	82.84	0.08

Applying the equation

$$r = \pm 0.8453 \frac{\sum |v|}{\sqrt{n(n-3)}}$$

to the results, the probable error is seen to be ±0.24.

Herzfeld's determinations do not seem therefore, to be of a very high order of accuracy. The calculation of solubilities to two places of decimals, as has been done in his published table is quite unjustified in view of the above probable error of ±0.24. Furthermore, the large temperature interval between 59°.4 and 99°.45, make the results at higher temperatures doubtful, as any error at the latter temperature would have an appreciable influence on the course of the curve.

The writer's results are in better agreement with those of Grut, as can be seen from the curves of Figure 34, although the latter's results are somewhat higher throughout. There seems to be little doubt that Herzfeld's figures are appreciably in error.

The solubility of sucrose at temperatures from 15° to 95°C. at intervals of 1° C, calculated by means of the equation from the writer's results, and expressed both as gms/100 gms solution and gms/100 gms water, are given in Table 20. These figures have been used for the work on velocity of crystallisation.

TABLE 20.

Solubility of Sucrose in Pure Solution.

Temp. °C.	Grams Sucrose per		Temp. °C	Grams Sucrose per	
	100 Soln.	100 Water.		100 Soln.	100 Water
15	65.63	191.0	56	73.45	276.6
16	65.80	192.4	57	73.67	279.8
17	65.97	193.9	58	73.88	282.8
18	66.14	195.3	59	74.10	286.1
19	66.31	196.8	60	74.32	289.4
20	66.48	198.3	61.	74.54	292.8
21	66.66	199.3	62	74.76	296.2
22	66.83	201.5	63	74.98	299.7
23	67.01	203.1	64	75.20	303.2
24	67.18	204.7	65	75.43	307.0
25	67.36	206.4	66	75.65	310.7
26	67.54	208.1	67	75.88	314.6
27	67.72	209.8	68	76.11	318.6
28	67.90	211.5	69	76.34	322.7
29	68.08	213.3	70	76.57	326.8
30	68.27	215.2	71	76.80	331.0
31	68.45	217.0	72	77.03	335.4
32	68.64	218.9	73	77.26	339.8
33	68.83	220.8	74	77.50	344.4
34	69.01	222.7	75	77.74	349.2
35	69.20	224.7	76	77.97	353.9
36	69.39	226.7	77	78.21	358.9
37	69.60	228.9	78	78.45	364.0
38	69.78	230.9	79	78.69	369.3
39	69.97	233.0	80	78.93	374.6
40	70.17	235.2	81	79.17	380.1
41	70.37	237.5	82	79.42	385.9
42	70.56	239.7	83	79.66	391.6
43	70.76	242.0	84	79.91	397.8
44	70.96	244.4	85	80.16	404.0
45	71.16	246.7	86	80.41	410.5
46	71.37	249.3	87	80.66	417.1
47	71.57	251.7	88	80.91	423.8
48	71.77	254.2	89	81.16	430.8
49	71.98	256.9	90	81.41	437.9
50	72.19	259.6	91	81.67	445.6
51	72.39	262.2	92	81.92	453.1
52	72.60	265.0	93	82.18	461.2
53	72.81	267.8	94	82.44	469.5
54	73.03	270.8	95	82.69	477.7
55	73.24	273.7			

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