

THE FREQUENCY OF NUCLEATION IN
A SUSPENSION OF GROWING CRYSTALS

A Thesis submitted for the Degree of
Doctor of Philosophy
in the Faculty of Engineering, University of London
by

MARK INIGO PHILLIPS
B.Sc., Dip.K.C.L., C.Eng., M.I.Chem.E.

E.R.D.E. Waltham Abbey

October 1972

SUMMARY

The frequency of nucleation in an agitated bed of ammonium perchlorate crystals has been studied using a continuous cooling crystallizer. The size distribution of the crystals obtained has been measured and fitted to a theoretical size distribution which allows for a variation in crystal growth rate with crystal size. From this and the value of the operating parameters the rates of growth and nucleation of the crystals have been calculated for a number of differing operating conditions.

The rate of growth has been found to be linear with supersaturation and linear with the fourth root of the power input to the crystallizer.

The rate of nucleation has been found to be proportional to the surface area of the suspended crystals, the rate per unit area being a simple power law with supersaturation and dependent on the agitation conditions as given by:

$$N_0 = 0.00293 \times S^{1.48} \times A \times N^2 \times D$$

The results are discussed in connection with the theories of secondary nucleation or crystal breeding, the conclusion being that the majority of the nucleation is caused by collision of the crystals with the impeller. The application of the results to large scale crystallizers is also discussed.

CONTENTS

ACKNOWLEDGMENTS		2
NOTATION		3
CHAPTER 1	PREVIOUS WORK	6
CHAPTER 2	THEORETICAL ANALYSIS	19
CHAPTER 3	EXPERIMENTAL TECHNIQUE AND PRELIMINARY EXPERIMENTS	33
CHAPTER 4	RESULTS	50
CHAPTER 5	DISCUSSION OF RESULTS	76
APPENDIX	THE COMPUTER PROGRAMME	92
BIBLIOGRAPHY		107

ACKNOWLEDGMENTS

I would like to express my gratitude to the following:

Dr. R.F.Strickland-Constable and Mr. R.P.Ayerst for their
continued encouragement and advice,
the Director, E.R.D.E. and the Superintendant, P.R. branch
for the provision of the research facilities,
Mr. M.J.Harper for his assistance in the writing of the
computer machine code procedures,
My wife, Mary, for her diligence and patience in typing
this thesis.

NOTATION

a	constant in mass transfer equation 2.1 constant in rate of growth equation 2.33 constant in power equation 4.1.2
a'	integration constant
A	surface area of suspended crystals
b	constant in mass transfer equation 2.1 constant in power equation 4.1.2
c	concentration of solution (wt%)
c _o	concentration of saturated solution
C	constant in equation 1.5
D	impeller diameter
D _L	solution diffusivity
F	rate of production
g	gravitational constant
ΔG	change in free energy to form a nucleus (homogeneous nucleation)
ΔG'	change in free energy to form a nucleus (heterogeneous nucleation)
k	mass transfer coefficient
k ₁	constant in growth rate equation 2.4
k ₂	constant in power equation 4.1.2
l	size of a crystal
$\bar{l}$	mean crystal size
L	size of a crystal after it has been growing for the mean retention time
m	exponent of supersaturation in nucleation rate equation 1.8 exponent of supersaturation in growth rate equation 2.4
n	exponent of crystal size in growth rate equation 2.4
N	impeller speed
N'	number of suspended crystals

N_o	rate of nucleation
P	power input
q	population density of crystals
q_o	population density of nuclei
r	"radius" of a crystal
r_c	critical "radius" of a crystal
R	gas constant
S	supersaturation
t	time
T	mean retention time temperature
v	molecular volume
V	volume of crystallizer
V_r	liquid-crystal relative velocity
W	weight of suspended crystals
W_l	weight of suspended crystals undersize of size l
x	uniformity factor in RRS size distribution
Z_l	cumulative weight fraction undersize of size l
Z_l'	cumulative weight fraction oversize of size l
α	volume shape factor of crystals
β	area shape factor of crystals
δ	constant in growth rate equation 2.36
θ	angle of contact between solution and crystal
μ	liquid viscosity
ρ	crystal density
ρ_L	liquid density
σ	liquid-solid surface free energy
τ	impeller torque

ϕ	constant in equation 1.6	
Re	impeller Reynolds Number	$\frac{D^2 N \rho}{\mu}$
Re _p	particle Reynolds Number	$\frac{1 V_r \rho}{\mu}$
Fr	Froude Number	$\frac{DN^2}{g}$
N	Power Number	$\frac{P}{D^5 N^3 \rho}$
Sch	Schmidt Number	$\frac{\mu \rho}{D_L}$
Sh	Sherwood Number	$\frac{k_L}{D_L}$

CHAPTER 1 PREVIOUS WORK

1.1	INTRODUCTION	7
	Homogeneous Nucleation	8
	Heterogeneous Nucleation	10
1.2	SECONDARY NUCLEATION	10
	Initial Breeding	11
	Needle Breeding	11
	Polycrystalline Breeding	12
	Collision Breeding	12
1.3	METHODS USED IN THE STUDY OF SECONDARY NUCLEATION	13
	Direct Counting	13
	Maximum Supersaturation	15
	Continuous Crystallizers	16

1.1 INTRODUCTION

It has long been recognized that the two main variables involved in the successful operation of crystallization equipment are the rate of growth and the rate of nucleation of the crystals. While both of these quantities can and have been measured in the laboratory for a number of substances the results have generally been specific to the laboratory equipment and of little use for the designer of large scale crystallizers. The measurement of these two rates under conditions which can then be applied to large scale crystallizers has taken place only recently, the work of Mullin and his co-workers (11,30,31) on the rates of growth in fluidised bed crystallizers being an example.

The crystallization process is essentially a two stage one requiring firstly the development or manufacture of an ordered cluster of solute molecules capable of growth, which will be referred to as a nucleus and secondly the growth of the nucleus to form a macrocrystal. For crystallization from aqueous solutions the nucleation process generally requires a higher driving force or supersaturation than the growth process and led Ostwald (35) to define his "metastable" and "labile" regions of a supersaturated solution. These were such that the rate of nucleus formation was insignificant in the "metastable" region and was measurable in the "labile" region, the growth process being possible in both regions. Nucleation under these conditions has been called homogeneous or primary nucleation and is analogous to droplet formation in supercooled vapours.

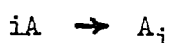
The presence of a foreign body such as dust or other solid fragments can cause nucleation to occur in the "metastable" region, Miers and Isaac (27) noting that the presence of glass chips caused nucleation of sodium nitrate solutions at much lower supercoolings than

was found using pure solutions in sealed glass phials. Nucleation under these conditions has been called heterogeneous nucleation.

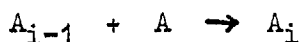
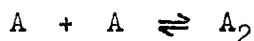
While these types of nucleation may be observed in the laboratory and in unseeded industrial crystallizers, in large scale continuous or seeded crystallizers the predominant form of nucleation is that which is due to the presence of the other crystals. Isaac (19) noted that the addition of crystals to a supercooled solution produced a shower of new crystals and that a further shower was produced on cooling the solution further. Nucleation under these conditions has been called secondary nucleation or crystal breeding and can occur at lower supersaturations than the other two types. Nevertheless a brief discussion of primary, homogeneous and heterogeneous nucleation will be included in the following.

HOMOGENEOUS NUCLEATION

The overall process of nucleus formation from solution can be represented by the equation



being the result of a series of bimolecular additions of molecules in the manner:



where i is the number of molecules or ions required to form a stable nucleus. The increase in solubility, c , of a crystal of size r is given by the Ostwald-Freundlich or Gibbs-Thomson equation which can be derived thermodynamically

$$\ln \frac{c}{c_0} = \frac{2\sigma v}{RTr} \quad 1.1$$

where c_0 is the solubility of a large particle, σ the interfacial Gibbs free energy, v the molecular volume, R the gas constant and T the absolute temperature. From this equation the critical size of a nucleus, r_c , which will be stable for a given solution concentration, c , can be expressed as

$$r_c = \frac{2\sigma v}{RT \ln (c/c_0)} \quad 1.2$$

Particles of a size smaller than r_c will dissolve, or enter into the series addition above to form a nucleus, while particles larger than r_c will grow to form crystals.

The change in free energy to form a nucleus of size r_c is given by

$$\Delta G = \frac{4}{3}\pi r_c^2 \sigma \quad 1.3$$

and substituting for r_c from equation 1.2 gives

$$\Delta G = \frac{16\pi\sigma^3 v^2}{3R^2 T^2 (\ln (c/c_0))^2} \quad 1.4$$

The rate of nucleation, N_0 , has been expressed as

$$N_0 = C \times \exp - \frac{\Delta G}{RT}$$

where C is a composite quantity and is only slightly temperature dependent.

On substituting for ΔG

$$N_0 = C \times \exp - \frac{16\pi\sigma^3 v^2}{3R^3 T^3 (\ln (c/c_0))^2} \quad 1.5$$

This equation predicts a high dependence of the nucleation rate on supersaturation and accounts for the 'explosive' formation of nuclei at a critical supersaturation corresponding to the transition from Ostwald's "metastable" region to the "labile" region. Mullin (28) and Melia (25) among others however have queried whether nucleation from

solution is ever truly homogeneous and capable of being described by the above equation. Although values of the interfacial free energy are difficult to determine, use of a reasonable estimated value will generally give values of the critical supersaturation that are orders of magnitude higher than those found in practice.

HETEROGENEOUS NUCLEATION

The presence of foreign particles or even the vessel surface can often induce nucleation at much lower levels of supersaturation than those required for homogeneous nucleation. Consequently the change in free energy on the formation of a nucleus heterogeneously, $\Delta G'$, must be lower than that for homogeneous nucleation:

$$\Delta G' = \phi \Delta G \quad 1.6$$

where the factor ϕ is less than unity. Volmer (49) considered the case of nucleation on a plane surface, where the angle of contact between the foreign surface and the crystal was θ , and obtained:

$$\phi = \frac{1}{4} (2 + \cos\theta)(1 - \cos\theta)^2 \quad 1.7$$

The nucleation rate equation has the same form as for homogeneous nucleation with the same 'explosive' dependence on supersaturation. It seems likely that for most substances crystallizing from aqueous solution heterogeneous nucleation has been observed and been mistakenly called homogeneous nucleation, Miers & Isaac (27) reporting in 1906 that by careful preparation of the solution in a sealed container nucleation did not occur in the "labile" region.

1.2 SECONDARY NUCLEATION

This type of nucleation has been known for many years, Isaac (19) in 1908 noting that "the introduction of crystals caused a dense shower to appear in the solution", and Ting & McCabe (48) in 1934 stating that "a seed crystal falling through a highly supersaturated solution leaves behind a trail of small seed crystals". The nucleation

has been characterised by Strickland-Constable and his co-workers who describe it as the breeding of nuclei.

INITIAL BREEDING

Strickland-Constable and Mason (47) reported that when an ordinary crystal is placed in a supersaturated solution a considerable number of crystals appear in the course of a few minutes. This nucleation occurred at low levels of supersaturation and was a once-and-for-all effect; hence the term initial breeding. It is explained by the presence on the surface of the crystal of crystallites which were produced either by the drying of the crystal or by mechanical abrasion of the crystal in the stock bottle. The nucleation disappears if the crystal is placed in an undersaturated solution for some time before being added to the supersaturated solution.

NEEDLE BREEDING

Under certain conditions of supersaturation a crystal, which has been pretreated so that there is no initial breeding, can grow needles or spikes from the ends of the crystal. If these break off they then produce fresh crystals; needle breeding. Strickland-Constable and Mason (47) and Mason and Strickland-Constable (22) found that if a crystal of magnesium sulphate heptahydrate were held on a glass rod and rotated in a supersaturated solution with a supercooling of less than 4°C the crystal grew normally. If the supercooling were greater than 4°C further crystals appeared in the solution. Observation of the crystals showed that at the higher supercooling a bundle of needles grew out of the end of the crystal and these were seen to break off under the rotational forces and grow as separate crystals.

It has been suggested by a number of Workers (Powers (37), Cayey and Estrin (13), Bransom, Brown and Heeley (8)) that there is an

"ordering" of solute molecules close to the surface of the crystal and that when these are removed by fluid shear they form a nucleus for subsequent crystal growth. Lal, Mason and Strickland-Constable (20) showed that it was possible to rotate a crystal of magnesium sulphate heptahydrate up to 4000 rpm without any nucleation taking place, provided the supercooling were less than 4°C . Above 4°C supercooling nuclei were produced as reported by Mason and Strickland-Constable. These results confirm that for magnesium sulphate heptahydrate fluid shear alone cannot produce nuclei unless assisted by needle or dendritic growth. Initial and needle breeding and the absence of any nucleation through fluid shear were also observed by Clontz and McCabe (15) whose results duplicate the findings of Lal, Mason and Strickland-Constable.

POLYCRYSTALLINE BREEDING

Mason and Strickland-Constable found that when potassium bromide was grown from aqueous solution under certain conditions of supersaturation and agitation the crystal did not grow as a single crystal but as a polycrystalline aggregate. This sometimes broke up spontaneously to give fresh crystals. This type of breeding differs from needle breeding in that in the latter the part of the crystal that breaks off to cause the breeding is part of the parent crystal lattice.

COLLISION BREEDING

Strickland-Constable and Mason reported that collision of a crystal with the walls of the vessel readily resulted in breeding even at low supersaturations. It is of major interest in that it can occur under conditions which will give perfect crystal growth while needle and polycrystalline breeding are associated with the growth of imperfect crystals. It will obviously be relevant to the growth of crystals in

industrial crystallizers where large numbers of crystals are kept under high agitation conditions with low levels of supersaturation - conditions necessary for the production of crystals of good quality and shape.

1.3 METHODS USED IN THE STUDY OF SECONDARY NUCLEATION

A variety of methods for studying secondary nucleation or collision breeding have been used and these can be summarised as follows:-

- 1) by direct counting of the number of crystals present after a suitable development time, especially when only one seed crystal is present;
- 2) by determining the maximum supersaturation a solution will tolerate when cooled at a constant rate in the presence of a crystal;
- 3) by measuring the number of crystals produced by a continuous crystallizer in unit time.

Methods 1) and 2) have the advantage that the experiments can be performed in relatively simple apparatus. Method 3) has the advantage that the conditions for the crystal nucleation are similar to those found in large scale crystallizers but the disadvantages that the apparatus must be well controlled and the interpretation of the results is more complicated.

DIRECT COUNTING

Lal, Mason and Strickland-Constable (20) performed two series of experiments with magnesium sulphate heptahydrate. In the first a crystal, suitably pretreated to eliminate initial breeding, was added to a flask at a given supersaturation which was then slowly stirred for a few seconds so that the crystal slid along the bottom of the flask. The stirring was then stopped and the crystallites produced were allowed

to develop for counting purposes. The results gave a marked dependence on supersaturation. In the second series of experiments a crystal was slid along the bottom of a tube at varying speeds and the number of crystals produced counted as previously. Again there was a marked dependence on supersaturation. Nucleation was also induced when a glass rod touched the parent crystal.

It was suggested that the nuclei were produced by attrition of the crystal as it slid along the flask or tube, and that the dependence on supersaturation was a reflection of the ability of a crystallite to survive in a solution of known supersaturation as given by the Gibbs-Thomson equation 1.1. At high supersaturations the critical size of a nucleus will be smaller and so more crystal fragments will appear as crystals after a suitable growth period.

Melia and Moffitt (26) performed similar experiments with a potassium chloride crystal mounted on a glass rod and found that nucleation did not occur until dendritic growth appeared on the crystal. Further the number of nuclei produced was proportional to the rotational speed of the crystal. They also showed that once crystals were produced they were themselves capable of producing further nuclei. While their results are consistent with needle breeding from the seed crystal, the fact that they did not differentiate between first and second generation nuclei makes the results difficult to interpret as to the effect of collisions.

Cayey and Estrin (13) used magnesium sulphate heptahydrate crystals either dropped into a flask or held on a glass rod. In the latter case the number of crystals produced remained constant for about thirty minutes and this suggests that they were observing initial breeding rather than collision breeding.

Clontz and McCabe (15) extended the experiments of Lal, Mason and Strickland-Constable (20) with magnesium sulphate heptahydrate and observed the effect of the energy of impact of either a rod-crystal collision or a crystal-crystal collision. The crystallites formed by the collision were swept away by a stream of supersaturated solution and allowed to develop in a tube away from the parent crystal. They found that the velocity of the solution past the crystal had no effect on the number of crystals obtained, the number of crystals produced was proportional to the area of contact and nearly twice as many crystals were obtained with crystal-crystal collisions as with rod-crystal collisions. Over the range of supersaturation investigated (about 5°C supercooling) they found that the number of crystals produced per unit area of contact was directly proportional to the supersaturation and directly proportional to the energy of contact.

In the discussion they suggest that in a large scale crystallizer the energy of crystal-crystal collisions is unlikely to be large enough to produce appreciable nucleation and that the majority of the nucleation will be produced by the much more energetic collisions of a crystal with the agitator or pump impeller.

MAXIMUM SUPERSATURATION

Nyvelt (33) made a number of simplifying assumptions to the Becker-Debring equation (equation 1.5) and obtained the following equation for the rate of nucleation:

$$N_0 = \text{constant} \times S^m \quad 1.8$$

If m is large and a solution is cooled at a constant rate, there will be a very rapid rise in the nucleation rate at a given supersaturation at which value the weight of material used in nucleus formation will be equal to the rate of formation of supersaturation.

The experiments consisted of cooling a stirred solution at differing constant rates and noting the maximum supersaturation that was obtained. A plot of the cooling rate against the maximum supersaturation on logarithmic co-ordinates gave a series of straight lines whose slope was "m". Nyvlt found that "m" had a value in the range 4-7 for a number of simple salts nucleating from aqueous solution. He also found that the slope of the line was not altered by the presence of the parent crystal although the maximum supersaturation obtained in that case was lower than in the absence of the crystal.

Mullin, Chakraborty and Mehta (29) used a similar technique with ammonium phosphate from aqueous solution. For unseeded solutions the value of "m" was 6.4, but for seeded solutions the value was 2.6.

Experiments of this type provide data on the nucleation process which is useful for the design of industrial crystallizers but are not specifically designed to throw light on the mechanism of the nucleation process.

CONTINUOUS CRYSTALLIZERS

This method consists of measuring the output or product crystals from a continuous crystallizer, the number of crystals produced in unit time being the nucleation rate.

Bransom, Dunning and Millard (10) crystallized RDX (sym-cyclo-trimethylenetrinitramine) from aqueous nitric acid by mixing nitric acid, saturated with RDX, and water in a continuous precipitator. The crystal size distribution was determined by a photosedimentometer and the nucleation rate obtained by extrapolating the number-size distribution function to zero size. They found a strong dependence on supersaturation and suggested the empirical equation

$$N_0 = \text{constant} \times S^3$$

Bransom, Brown and Heeley (8) similarly calculated the nucleation rate by using a photosedimentometer to determine the size distribution of the product crystals using magnesium sulphate heptahydrate. They found that the rate of nucleation was proportional to the surface area of the crystals in suspension in the crystallizer. Further the rate of nucleation per unit area of suspended crystals was linear with supersaturation after a threshold value had been reached.

Randolph and Rajagopal (40) set up an apparatus in which only very small crystals, less than 50 μm in size, could leave the crystallizer which was seeded with crystals in the size range 300-420 μm . These small crystals were analysed by a Coulter electronic particle counter and the nucleation rate found by extrapolating the number-size distribution curve to zero size. Using potassium sulphate they found that the rate of nucleation was proportional to the weight of crystals in suspension raised to the power 0.4, and decreased with an increase in supersaturation. They suggested that nucleation was occurring on active sites of the suspended crystals and that at high supersaturations, which will give high rates of crystal growth, these active sites are overgrown thus reducing the rate of nucleation.

Cise and Randolph (14) modified the apparatus of Randolph and Rajagopal in that the discharge from the crystallizer passed all crystals less than 150 μm , which were then analysed by a 14 channel Coulter counter. The crystallizer was seeded with about 1g of crystals in the size range 250-300 μm and the variation of the size of the product crystals with time determined. Their results showed that at the beginning of the experiment nuclei were produced by initial breeding and that after 30 to 40 minutes this had ceased and they were observing true secondary nucleation by collision breeding. They found that for potassium

sulphate the rate of nucleation increased with increasing supersaturation and increasing stirring rate. They found that the rate of nucleation was dependent on the surface area of the crystals in suspension and that as these grew with time the larger crystals produced proportionally more nuclei than when they were smaller. This may be due to the larger crystals falling to the bottom of the crystallizer, as they reported, and so experiencing more collisions as they slid along the bottom.

The experiments of Randolph and Rajagopal (40) and Cise and Randolph (14) were both made on a continuous crystallizer operating under non-steady state conditions and the subsequent analysis to obtain the nucleation rates is complex. This may explain the contradictory findings of the two series of experiments.

The theoretical analysis of a continuous crystallizer and a method for calculating the rate of nucleation are discussed further in the following chapter.

CHAPTER 2 THEORETICAL ANALYSIS

2.1	A THEORETICAL CONTINUOUS CRYSTALLIZER	20
2.2	METHOD OF CALCULATION	26
2.3	THE COMPUTER PROGRAM	29
2.4	APPENDIX	31

2.1 A THEORETICAL CONTINUOUS CRYSTALLIZER

The continuous-stirred-tank type of crystallizer lends itself to a mathematical treatment as the assumptions made in setting up the mathematical model are found to be true in the real crystallizer. Moreover these assumptions apply equally to large scale crystallizers as to laboratory-scale crystallizers so that data found in the latter should be suitable for scale-up to a larger unit. The assumptions are:-

- a) the suspension of crystals is perfectly mixed;
- b) the crystallizer is operating under steady state conditions;
- c) the number of crystals withdrawn from the crystallizer is equal to the rate of formation of nuclei and that the nucleus has negligible, but not zero, size;
- d) the crystals grow with uniform habit;
- e) the crystals withdrawn from the crystallizer are taken from the perfectly mixed suspension and are not subjected to any classification or size discrimination.

Mass transfer rates in liquid-solid systems can be correlated using an expression of the form:-

$$Sh = \text{constant} \times Sch^a \times Re_p^b \quad 2.1$$

Hixson and Knox (18) for example measuring the rates of growth of copper sulphate pentahydrate and magnesium sulphate heptahydrate found that 'a' had a value 0.6 and 'b' a value of 0.3. Replacing the dimensionless groups in equation 2.1 by their constituents gives:-

$$\frac{kl}{D_L} = \text{constant} \times \left(\frac{\mu \rho_L}{D_L} \right)^a \times \left(\frac{1V_r \rho_L}{\mu} \right)^b \quad 2.2$$

For a system at constant temperature the liquid parameters will be constant and the growth rate, which is related to the mass transfer

coefficient, k , by the equation:-

$$\frac{dl}{dt} = \text{constant} \times \frac{k}{\rho} \quad 2.3$$

can be expressed in the form of the general equation:-

$$\frac{dl}{dt} = k_1 S^m l^n \quad 2.4$$

where k_1 is a constant containing terms such as the liquid diffusivity and viscosity, the difference in density between the crystal and solution etc, S is the average supersaturation experienced by a crystal, and m and n are constants for any given system. From continuous stirred-tank-reactor theory Bransom (7) showed that the number of crystals, qdl , in a size range l to $l + dl$ of a growing crystal population decays exponentially with time:-

$$qdl = q_0 dl \cdot e^{-t/T} \quad 2.5$$

where q_0 is the population density of the nuclei and T the mean retention time. When dq/dt is constant, ie the rate of crystal withdrawal is equal to the rate of nucleus formation (condition c), Randolph and Larson (39) showed that:-

$$\frac{d}{dl} \left(q \frac{dl}{dt} \right) = - \frac{q}{T} \quad 2.6$$

and substitution for the rate of growth from equation 2.4 gives:-

$$\frac{d}{dl} \left(q k_1 S^m l^n \right) = - \frac{q}{T} \quad 2.7$$

Bransom (7) integrated this equation between the limits $t = 0$ and $t = t$ and obtained:-

$$qdl = a' \exp - (l/L)^{1-n} dl$$

However when the rate of growth is dependent on the size of the crystal Randolph (38) showed that the increment of crystal size dl in the population density varied with the size of the crystal and integrated equation 2.7 to obtain:-

$$qdl = a' l^{-n} \exp - (l/L)^{1-n} dl \quad 2.8$$

where a' is the integration constant and L the size of a crystal after it has been growing for the mean retention time and is given by:-

$$L = \left((1-n) k_1 S T \right)^{\frac{1}{1-n}} \quad 2.9$$

Equation 2.8 is the expression for the population density or number-size distribution function of the crystals and the total number of crystals in suspension, N' , is obtained by integrating equation 2.8 for all crystal sizes:-

$$\begin{aligned} N' &= V \int_0^{\infty} a' l^{-n} \exp - (l/L)^{1-n} dl \\ &= \frac{V a' L^{1-n}}{1-n} \end{aligned} \quad 2.10$$

the details of the integration being given in the appendix to this chapter. The lower limit of the integration should strictly be r_c , the critical size of a nucleus. However condition c) is that the nucleus has negligible size and the lower limit may be set to zero with no loss of accuracy.

From condition c) and the definition of the mean retention time the rate of nucleation, N_0 , is given by:-

$$N_0 = \frac{N'}{T} \quad 2.11$$

$$= \frac{V a' L^{1-n}}{(1-n)T} \quad 2.12$$

The weight of crystals in suspension is given by:-

$$W = V \alpha \rho \int_0^{\infty} l^3 q dl \quad 2.13$$

where α is a shape factor such that the volume of a crystal of size l is αl^3 and ρ the crystal density. Substituting the value of $q dl$ from equation 2.8:-

$$W = V \alpha \rho \int_0^{\infty} a' l^{3-n} \exp - (l/L)^{1-n} dl \quad 2.14$$

This integral was thought by Bransom (7) to be "intractable" and he made the simplifying assumption that n was zero. The integral is an example of the Gamma function which is defined by:-

$$\text{Gamma } (a) = \int_0^{\infty} z^{a-1} e^{-z} dz. \quad 2.15$$

For positive integer values of the argument, a , the integral can be integrated by parts to give the factorial function:-

$$\begin{aligned} \text{Gamma } (a) &= (a - 1) (a - 2) (a - 3) \dots 2.1 \\ &= (a - 1)!. \end{aligned}$$

The Gamma function is an extension of the factorial function using non-integer values of the argument, a . It is definite for all values of a except negative integers and values of the Gamma function with an argument between 0 and 1 can be found in books of statistical tables. Values with arguments outside this range can be evaluated using the recurrence relationship:-

$$\text{Gamma } (a) = a \text{ Gamma } (a - 1) \quad 2.16$$

until the final argument is within the range 0 to 1.

Equation 2.14 then becomes:-

$$W = V \alpha \rho a' \frac{L^{4-n}}{1-n} \text{Gamma} \left(\frac{4-n}{1-n} \right). \quad 2.17$$

On substituting for a' from equation 2.12:-

$$W = \alpha \rho N_0 T L^3 \text{Gamma} \left(\frac{4-n}{1-n} \right). \quad 2.18$$

The weight of crystals in suspension is also given by:-

$$W = F \sqrt{T} \quad 2.19$$

and combining equations 2.18 and 2.19

$$F = \alpha \rho N_0 L^3 \text{Gamma} \left(\frac{4-n}{1-n} \right). \quad 2.20$$

The weight of crystals in suspension up to size l is obtained by

integrating equation 2.14 between the limits $l = 0$ and $l = 1$:-

$$W_1 = V \rho \int_0^1 a l^{3-n} \exp - (l/L)^{1-n} dl. \quad 2.21$$

The cumulative weight percentage of crystals under size l is the ratio of the weight of crystals up to size l to the total weight of crystals in suspension

$$\begin{aligned} Z_1 &= W_1/W \\ &= \frac{\int_0^1 l^{3-n} \exp - (l/L)^{1-n} dl}{\int_0^\infty l^{3-n} \exp - (l/L)^{1-n} dl} \end{aligned} \quad 2.22$$

By altering the limits of the integral for the Gamma function equation 2.15 the incomplete Gamma function is obtained. Only two are of interest being defined by:-

$$\text{gamma}(a, x) = \int_0^x z^{a-1} e^{-z} dz. \quad 2.23$$

$$\text{Gamma}(a, x) = \int_x^\infty z^{a-1} e^{-z} dz. \quad 2.24$$

the different limits being denoted by the use of lower and upper case g's. They are complementary and it follows that:-

$$\text{gamma}(a, x) + \text{Gamma}(a, x) = \text{Gamma}(a) \quad 2.25$$

Again for positive integer values of the argument, a , the integrals can be integrated by parts to give:-

$$\text{gamma}(a, x) = \text{Gamma}(a) - e^{-x} \sum_{i=1}^{i=a} \frac{\text{Gamma}(a)}{\text{Gamma}(i)} x^{i-1} \quad 2.26$$

$$\text{Gamma}(a, x) = e^{-x} \sum_{i=1}^{i=a} \frac{\text{Gamma}(a)}{\text{Gamma}(i)} x^{i-1} \quad 2.27$$

The incomplete Gamma functions are definite for all positive values of 'x' and all values of 'a'.

Equation 2.22 is therefore the ratio of the incomplete to the complete Gamma functions and can be evaluated by graphical integration, the method used by Bennett (6). Pearson (36) has tabulated values of this ratio for various arguments and limits, a and x, and this method was used by Ayerst and Phillips (5) when equation 2.22 becomes:

$$Z_1 = \text{gamma} \left(\left(\frac{4-n}{1-n} \right), \left(\frac{1}{L} \right)^{1-n} \right) / \text{Gamma} \left(\frac{4-n}{1-n} \right) \quad 2.28$$

Equation 2.22 can also be evaluated by numerical methods using the complementary function, ie the cumulative weight percentage oversize of size 1

$$Z_1' = \text{Gamma} \left(\left(\frac{4-n}{1-n} \right), \left(\frac{1}{L} \right)^{1-n} \right) / \text{Gamma} \left(\frac{4-n}{1-n} \right) \quad 2.29$$

which can be calculated using the continuous fraction (2):-

$$\text{Gamma} (a, x) = e^{-x} x^a \left(\frac{1}{x+} \frac{1-a}{1+} \frac{1}{x+} \frac{2-a}{1+} \frac{2}{x+} \dots \right) \quad 2.30$$

by any standard method.

The special case in which n is zero corresponds to McCabe's ΔL law (21) and equation 2.22 then becomes:-

$$Z_1 = 1 - \left[\exp - (1/L) \right] \left(1 + \frac{1}{L} + \frac{1}{2} \left(\frac{1}{L} \right)^2 + \frac{1}{6} \left(\frac{1}{L} \right)^3 \right) \quad 2.31$$

and the complementary function becomes:-

$$Z_1' = \left[\exp - (1/L) \right] \left(1 + \frac{1}{L} + \frac{1}{2} \left(\frac{1}{L} \right)^2 + \frac{1}{6} \left(\frac{1}{L} \right)^3 \right) \quad 2.32$$

Equation 2.31 was obtained by Saeman (45) and also Robinson and Roberts (41) as the solution for a single crystallizer in the general equation given for any number of crystallizers operating in series.

Matz, using the empirical Rosin, Rammler and Sperling (RRS) distribution:

$$Z_1' = \exp - (1/\bar{l})^x \quad 2.33$$

where $\bar{l}$ is the mean size of the crystal distribution and x the uniformity factor, has suggested (23) that if the rate of crystal growth is inversely proportional to the crystal size the uniformity factor is two. He has shown (24) that the data of Ayerst and Phillips (5) for the size distribution of ammonium perchlorate from a continuous crystallizer agreed well with a uniformity factor of two.

A fuller analysis of a continuous crystallizer has been given by Randolph and Larsen (39) who investigated the transient responses to changes in operating variables and by Nyvlt and Mullin (34) who examined the "steady un-steady" state of a continuous crystallizer where under certain operating conditions a continuous crystallizer will set up steady oscillations.

2.2 METHOD OF CALCULATION

If the dependence of the rates of growth and nucleation with supersaturation were known together with the particle and fluid dynamics of the system equations 2.9 and 2.20 would define the operation of the crystallizer and equation 2.22 would give the size distribution of the crystals in suspension. If condition e) were satisfied equation 2.22 would also give the size distribution of the product crystals.

Conversely, by measuring the size distribution of the product crystals and that of the suspended crystals, together with the values of the operating parameters, the values of the rates of growth and nucleation can be calculated from equations 2.9, 2.20 and 2.22 and their dependence on supersaturation and other operating conditions determined.

An alternative technique has been used by Canning and Randolph (12)

who extrapolated the population density or number-size distribution function to zero size to calculate the population density of the nuclei and hence the rate of nucleation. If 'n' is zero a plot of log (population density) against crystal size will be a straight line of slope $-dl/dt$ and intercept q_0 . If 'n' is not zero but say 0.1 the semi-log plot gives an infinite intercept at zero size and Canning and Randolph rejected the form of the growth rate equation 2.4 and replaced it by a polynomial expression:-

$$\frac{dl}{dt} = \left(\frac{dl}{dt} \right)_0 \left(1 + a_1 l + a_2 l^2 + \dots a_n l^n \right), \quad 2.34$$

where $(dl/dt)_0$ is the growth rate of a nucleus, which they simplified to

$$\frac{dl}{dt} = \left(\frac{dl}{dt} \right)_0 (1 + a_1 l). \quad 2.35$$

Abegg, Stevens and Larsen (1) have suggested a similar growth rate expression:-

$$\frac{dl}{dt} = \left(\frac{dl}{dt} \right)_0 (1 + a_1 l)^Y. \quad 2.36$$

However we have assumed that the nucleus does not have zero size, condition c), so that while the population density of the nuclei may be large, if 'n' is not zero, it will not be infinite. Further, integration of the population density to give the total number of crystals, gives a finite result and equation 2.10 is valid for all values of 'n' less than unity. Further nucleation rates calculated by equations 2.9, 2.20 and 2.22 will be finite and valid for all values of 'n' less than unity.

As the population density is generally calculated by interpolating the crystal weight-size distribution, it would seem more logical to use this directly, using equations 2.9, 2.20 and 2.22, rather than the method of Canning and Randolph in order to calculate the rates of growth and nucleation.

As L is raised to the third power in equation 2.20, then its value must be known with some certainty if the rate of nucleation is to be calculated with any degree of accuracy. The method used by Ayerst and Phillips (5) in which n was assumed to be zero and L found from the mean aperture of the size distribution of the product crystals is not very satisfactory as it is weighted towards the centre of the size distribution and ignores the upper and lower quartiles of the size distribution. A superior method is to perform a least squares minimization of equation 2.22 on all the experimental data in which all points on the distribution curve would be taken into account.

The process of minimization is to find values for the parameters L and n in equation 2.29 such that the sum of the squares of the differences between the experimental and calculated size distributions is a minimum. The technique described by Coggan (16), based on the Fletcher and Powell (17) method can be summarised as:-

- guess the initial values of the parameters (P_0);
- calculate the sum of the squares of the errors (S_0);
- 1: estimate the length and direction of a step in the parameters that will include the minimum (S_j);
- take this step (P_1);
- check that these values are within bounds;
- calculate the sum of the squares of the errors (S_1);
- determine whether the minimum lies between P_0 and P_1 ;
- interpolate the minimum (P_2);
- check that these values are within bounds;
- calculate the sum of the squares of the errors (S_2);
- check that $S_0 > S_2 < S_1$;
- set $P_0 = P_2$, $S_0 = S_2$ and return to 1 unless the conditions for leaving the loop are satisfied.

2.3 THE COMPUTER PROGRAM

In order to perform the necessary calculations a computer program was written in Algol 60 for operation on the Elliot 903 computer installed at E.R.D.E. By means of checks built into the program it was clear that the majority of the computer time was spent calculating the incomplete gamma function and the Algol procedure was rewritten as an Elliot 903 series machine code procedure reducing the overall time for the minimization by a factor of 3. The final version of the program contains the following procedures:-

lgamma	machine code procedure for calculating the logarithm of the complete Gamma function.
gammaa	machine code procedure for calculating the incomplete Gamma function.
ifl2 and ifl3	machine code procedures for checking the operation of the minimization technique.
print5	for printing any number to five significant figures
copy	for copying values
invertgamma	for calculating the "inverse" of the incomplete gamma function
solvex	for calculating the zero of an implicit function using a binary search
usemodel	for calculating the theoretical size distribution
constraints	for checking that the values of L and n are within bounds
crit	for calculating the sum of the squares of the errors
diff	for differentiating the objective function with respect to the parameters P at the point S
doublefit	for fitting the values of the two parameters L and n.

A copy of the program in full is given in the Appendix.

The program reads in the title and the experimental data and calculates the best value of L (BIGL), assuming n to be zero, for the size distribution of both the suspended crystals and the product crystals and plots the data points and the size distribution curves. If the two values of L differ by less than 10% the best values of L and n for the suspended crystals are calculated using as the initial guesses BIGL and 0 for L and n , and the size distribution curve is plotted.

APPENDIX TO CHAPTER 2

General solution of $\int_0^v x^r \exp - (x/a)^2 dx$

Substituting: $z = (x/a)^q$

then $x = az^{1/q}$

and $dx = \frac{a}{q} z^{\frac{1-q}{q}} dz$

When: $x = v \quad z = (v/a)^q$

and the integral becomes:

$$\int_0^{(v/a)^q} a^r z^{r/q} e^{-z} \frac{a}{q} z^{\frac{1-q}{q}} dz = \frac{a^{r+1}}{q} \int_0^{(v/a)^q} z^{\frac{r+1-q}{q}} e^{-z} dz$$

Now: $\int_0^x x^p e^{-x} dx = \text{gamma}(p+1, x)$

and the integral then becomes:

$$\frac{a^{r+1}}{q} \text{gamma}\left(\frac{r+1}{q}, \left(\frac{v}{a}\right)^q\right)$$

$$1: \int_0^\infty l^{-n} \exp - (l/L)^{1-n} dl = \frac{L^{1-n}}{1-n} \text{gamma}\left(\frac{1-n}{1-n}\right) \quad 2.7$$

$$2: \int_0^\infty l^{3-n} \exp - (l/L)^{1-n} dl = \frac{L^{4-n}}{1-n} \text{gamma}\left(\frac{4-n}{1-n}\right) \quad 2.11$$

$$3: \int_0^1 l^{3-n} \exp - (l/L)^{1-n} dl = \frac{L^{4-n}}{1-n} \text{gamma}\left(\frac{4-n}{1-n}, \left(\frac{1}{L}\right)^{1-n}\right) \quad 2.17$$

4: When $n = 0$:

$$\int_1^{\infty} l^3 \exp - (l/L) dl = L^4 \left\{ 3! - e^{-(1/L)} \sum_{i=1}^{i=4} \frac{3!}{(i-1)!} \left(\frac{1}{L} \right)^{i-1} \right\}$$

$$\text{from 2: } \int_0^{\infty} l^3 \exp - (l/L) dl = L^4 \text{ Gamma}(4)$$

$$= 6L^4$$

$$\therefore \frac{\int_1^{\infty} l^3 \exp - (l/L) dl}{\int_0^{\infty} l^3 \exp - (l/L) dl} = 1 - e^{-(1/L)} \left\{ 1 + \frac{1}{L} + \frac{1}{2} \left(\frac{1}{L} \right)^2 + \frac{1}{6} \left(\frac{1}{L} \right)^3 \right\} \quad 2.19$$

CHAPTER 3 EXPERIMENTAL TECHNIQUE AND PRELIMINARY EXPERIMENTS

3.1	INTRODUCTION	34
3.2	APPARATUS	34
3.3	MEASUREMENT OF SUPERSATURATION	37
3.4	MEASUREMENT OF POWER INPUT	37
3.5	MEASUREMENT OF SIZE DISTRIBUTION	40
3.6	THE CRYSTAL HABIT AND SHAPE FACTORS	41
3.7	OPERATING PROCEDURE	41
3.8	TESTS ON THE FEED STOCK FILTER	44
3.9	TEST OF THE SIZE DISTRIBUTION	45

3.1 INTRODUCTION

Earlier work (4) had shown that valuable results could be obtained using a laboratory crystallizer of 4l capacity, in which measurements were made with a large population of crystals and differences between individual crystals were insignificant. It was hoped that the apparatus would provide quantitative information on the nucleation processes but because of the complexity of the system and the time dependence of the batch crystallizer the results were only of a qualitative nature.

gh / As a continuation of the pilot-scale crystallizer work (5) the apparatus was to be a small scale continuous cooling crystallizer in which the throughput, weight of crystals in suspension, supersaturation and agitation conditions could be varied and determined and their effect on the rate of nucleation found. Ammonium perchlorate was used as the crystallizing substance as it was readily available in a high state of purity, its saturation concentrations had been determined (3) and it continues to play an important part in the work of E.R.D.E.

3.2 APPARATUS

The apparatus consisted of a glass crystallizing vessel fitted with four polished equally spaced stainless steel baffles and a cooling jacket. The jacket was preferred to a cooling coil in order to reduce the possibility of heterogeneous nucleation on the cold surface. The top of the vessel was ground flat and a perspex lid with a silicone rubber gasket sealed the vessel in order to minimize evaporation from the liquid surface with the resulting possibility of nucleation at the supersaturated surface.

The vessel was agitated by either of two geometrically similar six bladed turbine impellers, the diameters of which were approximately one half and one third that of the vessel. The impeller was driven by a 100W (1/4hp) motor and the speed varied by a variable autotransformer powered

from a stabilised mains source. The motor was clamped in a sub-frame which was free to move in a stationary frame being mounted in air pressure bearings, the lower being a radial and thrust bearing and the upper a radial bearing. The air supply to the bearing was from a 5.6 kN/m^2 (80 psig) source through a filter-dehumidifier unit and was interlocked with the power to the motor so that the bearing had to be pressurized before the motor could be brought into operation.

Cooling water for the crystallizer was from a Townson and Mercer thermostat bath being recirculated by a Stewart-Turner No 12 centrifugal pump controlled by a variable autotransformer. The thermostat bath was controlled by a thermistor bridge unit to an accuracy of better than $\pm 0.01^\circ\text{C}$.

So that runs of long duration could be performed it was decided to use a recirculation of the feed solution and the crystallizer overflow through a feed stock tank. This was of stainless steel mounted in a second Townson and Mercer thermostat bath and was agitated by a twin propeller stirrer driven by a small induction motor. The feed solution was pumped through the crystallizer by a positive displacement pump having first been filtered through a No 3 porosity sintered glass filter. The pump used initially was a Watson-Marlow peristaltic pump with neoprene rubber as the pumping tube. Trials with water showed that the hysteresis of the rubber, and therefore the pumping rate, varied with time and the pump was replaced by a stainless steel Mono pump type 7B driven by a 80W ($\frac{1}{2}$ hp) motor through a reduction gearbox. The speed of the pump was varied by a solid state speed variator powered from the stabilised mains source. The overflow from the crystallizer was returned direct to the feed stock tank which contained an excess of ammonium perchlorate crystals to keep the concentration of the feed stock tank constant.

The apparatus is shown diagrammatically in fig 3.1 and a photograph

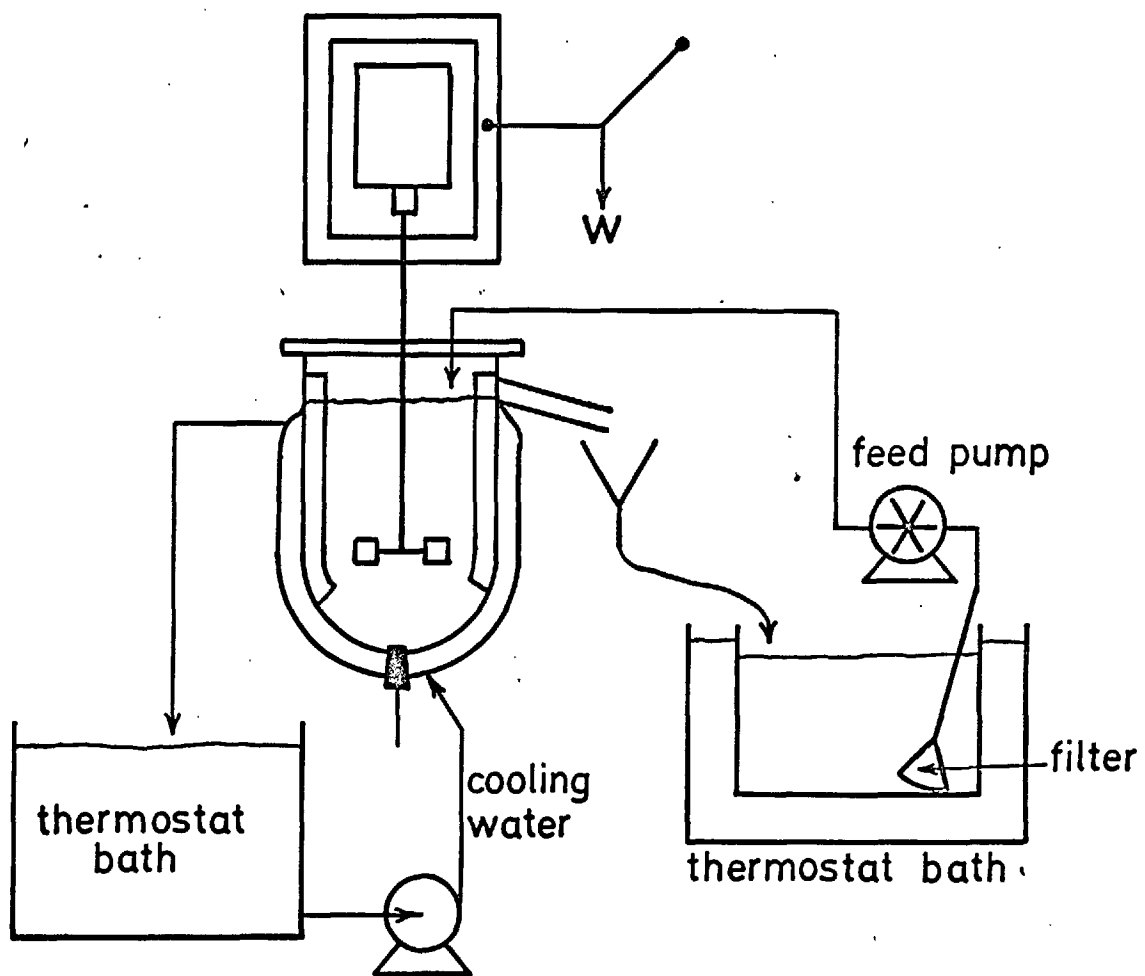


Fig3.1 Diagram of apparatus

showing the layout is fig 3.2, the principal dimensions being set out in Table 3.1.

3.3 MEASUREMENT OF SUPERSATURATION

The definition of supersaturation used is

$$S = \frac{c - c_0}{c_0}$$

where c is the concentration of the solution and c_0 the equilibrium or saturation value of the concentration, both concentrations being expressed as grams solute per 100 grams of solution. The solution concentration was determined by evaporation of a known weight of solution to dryness at 105°C, the method used by Ayerst & Phillips (3). The saturated concentration was found by measuring the temperature of the solution with a mercury in glass thermometer, calibrated against an NPL certificated thermometer, and using a polynomial interpolation of the data given by Ayerst & Phillips.

3.4 MEASUREMENT OF POWER INPUT

The power output from a motor is given by

$$P = 2\pi N \tau \quad 3.4.1$$

where N is the rotational speed of the motor and τ the output torque, and in order to determine the power of a motor both the speed and the torque must be measured.

The speed of the stirrer motor was measured by observing the stationary patterns produced by a strobotorch calibrated against the mains electricity frequency. As the air bearing suspension had a very low resistance to turning the torque applied to the stirrer was given by the restraining force at a point on the frame holding the motor.

The first method tried was to make an air bearing pulley with again very low resistance to turning so that the restraining force would be the

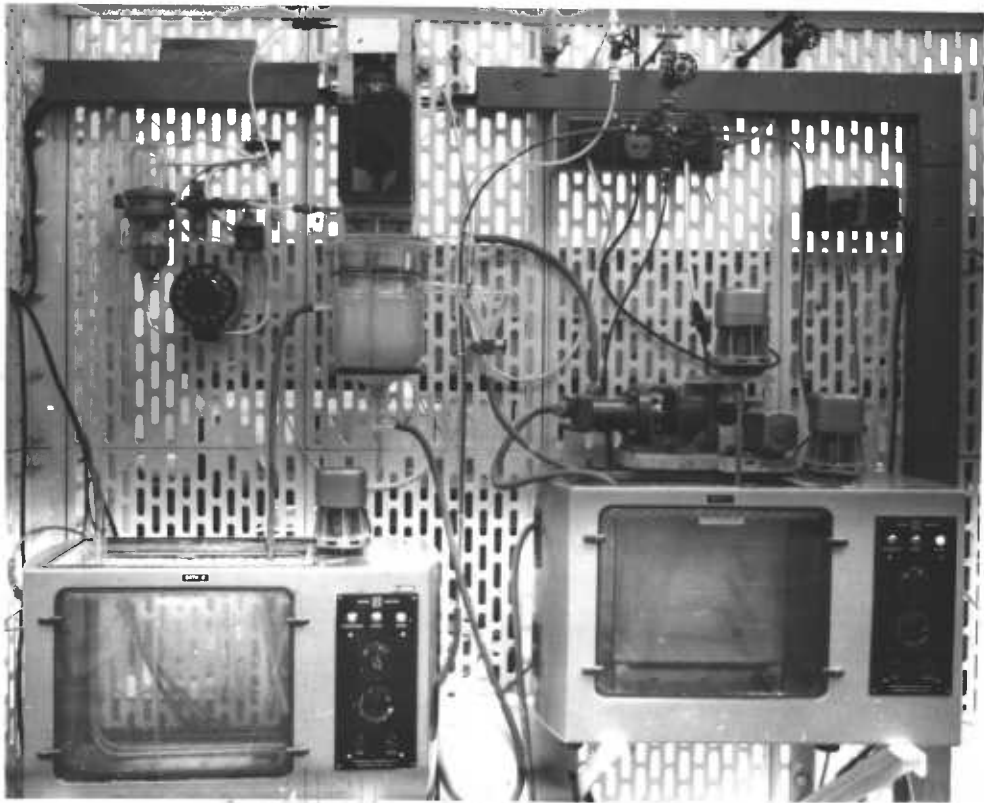
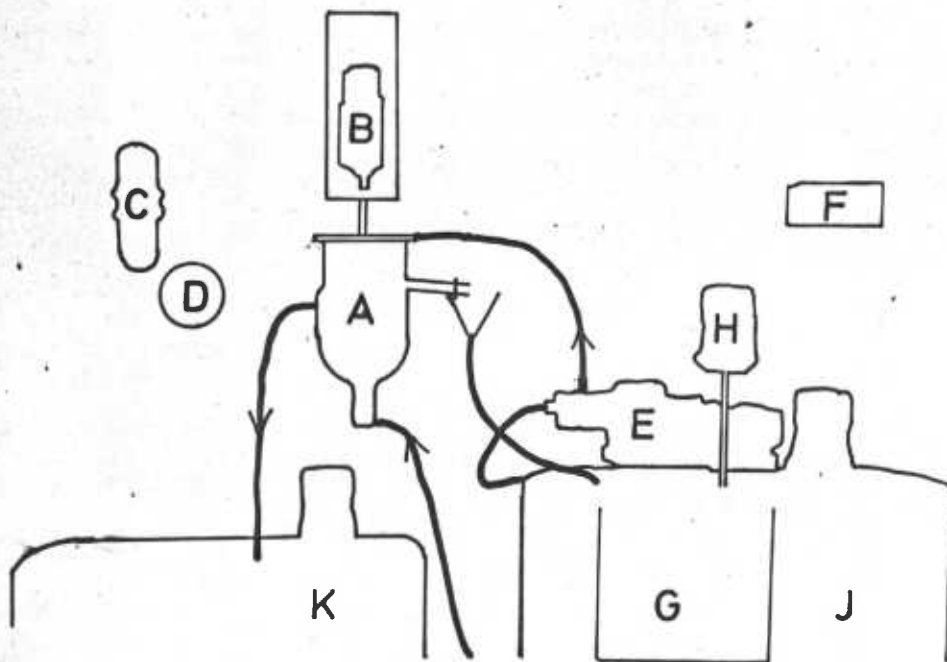


Fig 3.2 Layout of apparatus



- A crystallizer
- B stirrer motor and support frame
- C air filter and dehumidifier
- D stirrer motor autotransformer
- E feed solution pump
- F feed solution pump variator
- G feed solution stock tank
- H feed solution stock tank stirrer
- J feed solution thermostat bath
- K cooling water thermostat bath

TABLE 3.1 PRINCIPAL DIMENSIONS OF CRYSTALLIZER

Volume of crystallizer	2.36 l	
Internal diameter of crystallizer	15.0 cm (6")	
Impellers:	Half Diameter	Third Diameter
Overall diameter	7.41 cm	4.98 cm
Diameter of disc	5.69 cm	3.80 cm
Blade height	1.48 cm	1.00 cm
Blade width	1.82 cm	1.25 cm
Number of blades	6	
Diameter of shaft	0.97cm ($\frac{3}{8}$ ")	
Baffle width	1.9 cm	
length	13.5 cm	
Immersion of impeller	11.0 cm	

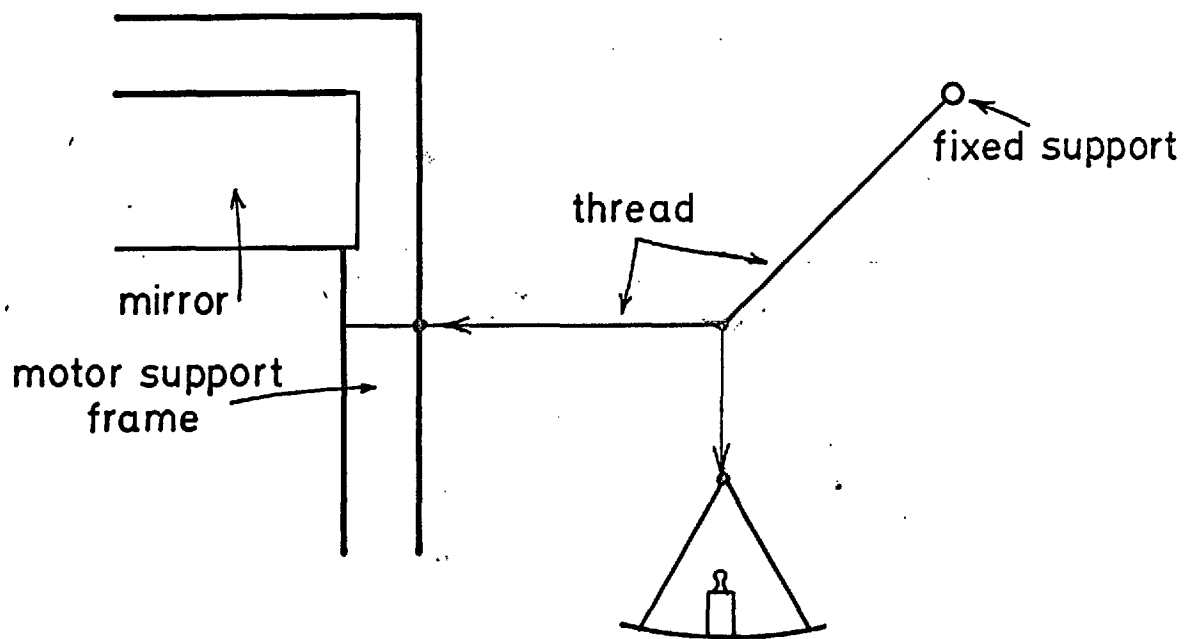
weight of a known mass. While this looked promising it was unsuccessful as the air bearing was unable to work effectively under the radial loads that were applied.

The method eventually used was the arrangement of terylene thread shown diagrammatically in fig 3.3. The angles between the threads were set by adjusting the lengths of the threads with the air to the bearing on the motor frame switched off and the location of the frame determined by an optical lever. With the motor running the weight required was estimated and adjusted so that the motor frame was in the calibration position as given by the optical lever. By this means the restraining force was measured with an accuracy of $\pm 1g$.

The thread arrangement is not shown in the photograph of the apparatus (fig 3.2) as it was not reassembled after the apparatus was removed to another laboratory. The mirror forming the moving part of the optical lever can be seen at the top of the frame clamping the stirrer motor and the fixed support is to the right of the mirror on the main framework.

3.5 MEASUREMENT OF SIZE DISTRIBUTION

The crystals under test were separated from the supernatant liquid by rapid vacuum filtering through a sintered glass filter heated to 30°C. The crystals were then washed with ethanol saturated with ammonium perchlorate and finally diethyl ether. After drying in an oven at 105°C the crystals were transferred to a set of laboratory 8" diameter stainless steel sieves to BS 410 : 1969 which were vibrated by an Endecott sieve shaker for 25 minutes. The cumulative weight retained on each sieve was determined by transferring the crystals to a tared container after cleaning the sieve mesh with a brass wire brush.



Effective radius of restraining force 8.89 cm

Fig 3.3 Thread arrangement for measuring restraining force

3.6 THE CRYSTAL HABIT AND SHAPE FACTORS

The size of a crystal, l , used in section 2 was an arbitrary dimension and shape factors were defined such that the volume and area of a crystal were given by:-

$$\text{volume} = \alpha l^3$$

$$\text{area} = \beta l^2$$

Ammonium perchlorate is an orthorhombic crystal crystallizing from aqueous solution in a rhombohedral habit, typical crystals being shown in fig 3.4. These crystals were retained in the mesh of a 300 micron (52 mesh) sieve after a sieving analysis and shown how the size of the crystals is related to the sieve aperture.

The idealised shape of a crystal is shown in fig 3.5, the size of the crystal, l , being the length of the side of the rhombus and also the "thickness" of the crystal. The area and volume of the crystal are then:-

$$\text{area} = (2 \sin 75^\circ \times 4) l^2$$

$$\text{volume} = \sin 75^\circ l^3$$

and the shape factors:-

$$\alpha = 0.966$$

$$\beta = 5.932$$

$$\frac{\beta}{\alpha} \sim 6$$

3.7 OPERATING PROCEDURE

The feed stock tank was filled with a solution of ammonium perchlorate in distilled water saturated at the temperature of the thermostat bath with an excess of ammonium perchlorate in the tank. The sintered glass filter, previously cleaned in chromic acid and washed free of acid with distilled water, was filled with solution by suction and connected to the tube leading to the feed pump which was then switched on. When the crystallizer was full the air to the stirrer motor support frame was switched on and the stirrer motor set to the required speed. The cooling

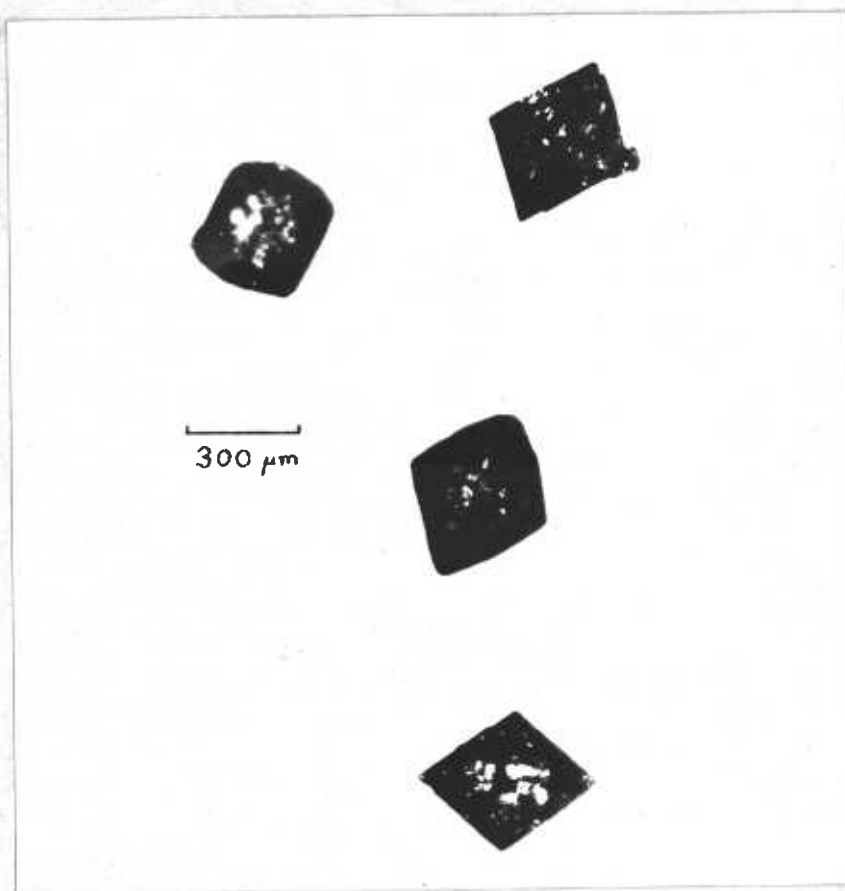


Fig 3.4 Typical crystals

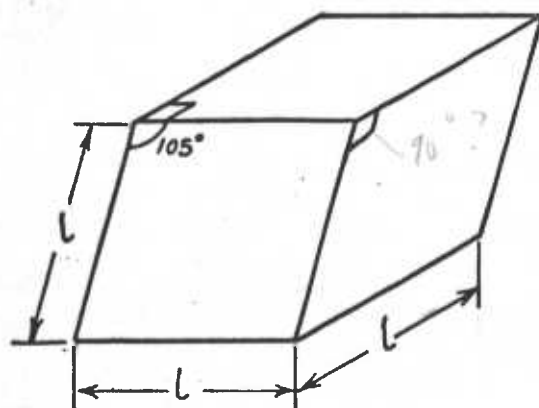


Fig 3.5 Ideal crystal shape

water recirculation pump was then started and the speed of the feed pump set to the required value. After an hour or so the speed of the stirrer motor was again checked and the weights added to the pan to obtain the required restraining force. (See section 3.4). The preliminary experiments showed that no difference in the restraining force required when the crystallizer was operating and when it was filled with water could be detected and on removing the apparatus to another laboratory the measurement of the restraining force was discontinued, the value used being that obtained with water in the crystallizer.

After about six hours running a sample of the solution was taken from the crystallizer overflow and a portion of the sample decanted into a tared flask for the determination of the supersaturation, as described in section 3.3. A further sample was taken from the crystallizer overflow, the time for collection being noted with a stop watch, and the crystals filtered off. The feed pump and cooling water recirculation pump were stopped simultaneously and the contents of the crystallizer dumped into a 3l beaker, the crystals again being filtered off. The stirrer motor was switched off just before air entrainment started. Both lots of crystals were treated as described in section 3.5 and their size distributions measured. At first a half set of sieves in the range 1200 - 75 μ m (14 to 200 mesh) was used but a full set of sieves was used for later runs as these became available.

The crystallizer and feed pump were washed in water ready for the next experiment and the sintered glass filter cleaned in chromic acid.

3.8 TESTS ON THE FEED STOCK FILTER

As the feed solution was from a stock tank containing crystals it is inevitable that crystals of nuclear proportions will pass through the sintered glass filter and grow into macro crystals once inside the

crystallizer. To check the effectiveness of the filter the feed pump was started and the feed solution returned direct to the feed stock tank. After two hours 75 ml samples of the feed solution were taken in glass conical flasks previously cleaned in chromic acid and then cooled to 1°C below the temperature of the feed solution. After 30 minutes the crystals were filtered, dried and counted, the mean of six determinations being 150 crystals per flask.

As a blank six 75 ml samples of the feed solution were taken and heated 5°C for 30 minutes before cooling to 1°C below the saturation temperature. No nucleation was observed after 30 hours and five of the six flasks had nucleated after 48 hours with one large crystal in each.

The crystals obtained in the first experiments were clearly the result of nuclei passing through the sintered glass filter. The rate of pumping the feed solution was typically 10 ml/s so nuclei were being added to the crystallizer at typically 20 s^{-1} . The rates of nucleation measured in the crystallizer were of the order of three orders of magnitude greater than this and the effect of nuclei passing through the filter could be ignored.

3.9 TEST OF THE SIZE DISTRIBUTION

The crystallizer was set in operation as described in section 3.6. After about four hours running a sample of the product crystals was taken and analysed for size distribution as described in section 3.5. After sieving the fraction less than $105\text{ }\mu\text{m}$ was further analysed using a Sharples micromerograph, an instrument using an air elutriation technique. The results are set out in Table 3.2 and shown graphically in fig 3.6.

A least squares fit of the sieving analysis was made as described in section 2 using both the incomplete Gamma function and the RRS

TABLE 3.2 SIZE ANALYSIS

	Crystal Size	wt.retained	cum.wt. retained	cum. %
	(μm)	(g)	(g)	
<u>Sieving</u>	850		.0258	.589
	600		.3215	7.338
	420		.9780	22.322
	300		2.1688	49.500
	210		3.3648	76.797
	150		3.8929	88.851
	105		4.2815	97.720
<u>Micromerograph</u>	86	.0560	4.3375	98.998
	64	.0604	4.3512	99.311
	54	.0761	4.3576	99.457
	47	.0790	4.3605	99.523
	43	.0814	4.3629	99.578
	34	.0861	4.3665	99.660
	30	.0872	4.3687	99.710
	22	.0901	4.3716	99.776
	17	.0919	4.3734	99.817
	11	.0955	4.3770	99.900
	8	.0978	4.3793	99.952
	6	.0993	4.3808	99.986
	4	.0999	4.3814	100.00
	3	.0999	4.3814	100.00

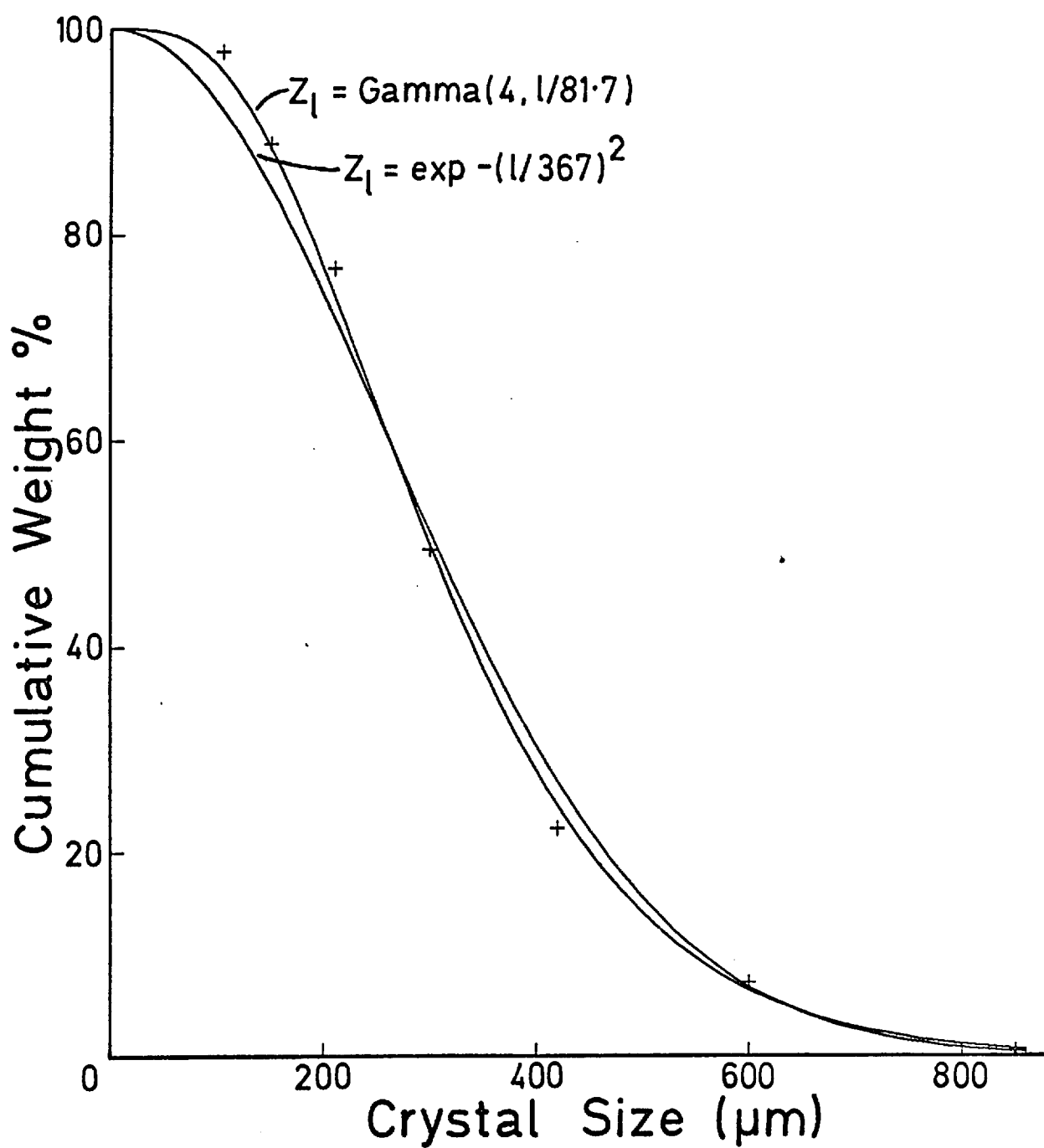


Fig 3.6 Test of Size Distribution

median/ distribution described by Matz (24). These least squares fits are the lines in fig 3.6 (Gamma (4,1/81.7) showing that "n" is zero and "L" 81.7 μm , and that the mean crystal size, $\bar{L}$, is 367 μm) and show that for large crystal sizes the RRS distribution is a tolerable description of the size distribution. This is because the exponential term in the incomplete Gamma function will be dominant at large crystal sizes and will therefore approximate to the RRS distribution. It is at low crystal sizes that the two equations differ and this is shown in fig 3.7, where the results from the micromerograph and the result from the finest sieve in the sieving analysis are shown together with the curves in fig 3.6 using enlarged scales. Because of the inaccuracies of the micromerograph the results do not lie on the line of the incomplete Gamma function, but this is a better description of the size distribution than the RRS distribution.

Further the micromerograph gave results to a crystal size of 6 μm , thus allaying the fears of Canning and Randolph (12) about the validity of the incomplete Gamma function at small crystal sizes. The departure of the data points from the incomplete Gamma function shown in fig 3.7 may be due to a change in the value of n in the growth rate equation at small crystal sizes, as found by Cise and Randolph (14) for potassium sulphate, but the experimental error of the micromerograph results is too large to make any positive conclusions.

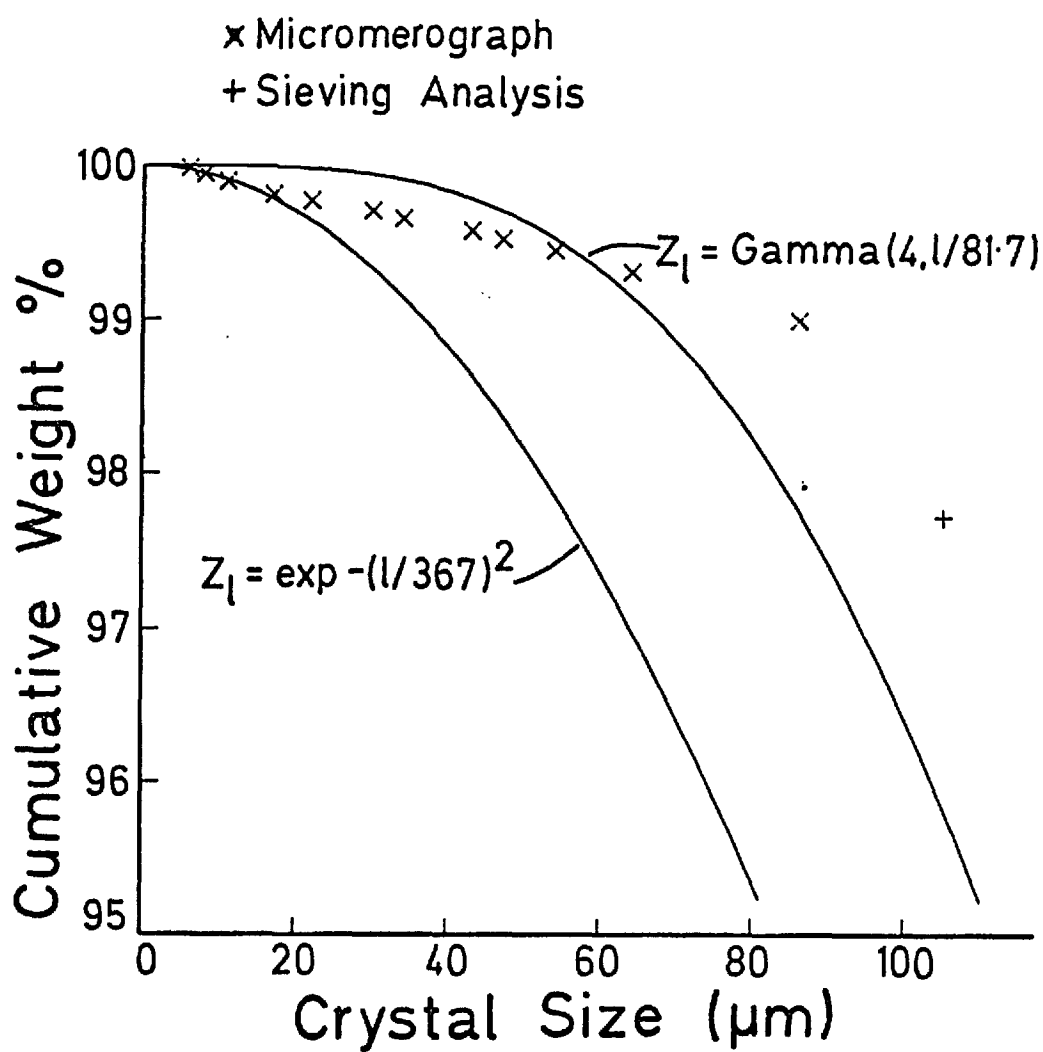


Fig 3.7 Micromerograph Results

CHAPTER 4 RESULTS

4.1	THE AGITATION CONDITIONS	51
4.2	CRITERIA FOR ACCEPTING THE RESULTS OF A RUN	55
4.3	THE SIZE DISTRIBUTION	55
4.4	THE VALUE OF "n"	60
4.5	THE RATE OF GROWTH	60
4.6	THE RATE OF NUCLEATION	64
4.7	SUMMARY OF RESULTS	73

4.1 THE AGITATION CONDITIONS

The power requirements of an impeller for a system of known and constant geometry will be some function of the impeller diameter and speed, D and N , the viscosity and density of the liquid, μ and ρ_L , and the gravitational constant, g :-

$$P = f_n(D, N, \mu, \rho_L, g) \quad 4.1$$

This equation can be rearranged into terms containing only dimensionless groups:-

$$\frac{Pg}{N^3 D^5 \rho_L} = k_2 \left(\frac{D^2 N \rho_L}{\mu} \right)^a \left(\frac{DN^2}{g} \right)^b \quad 4.2$$

which is more usually seen in its abbreviated form:-

$$N_p = k_2 Re^a Fr^b \quad 4.3$$

The Reynolds number, Re , is a measure of the viscous forces acting on the liquid and the Froude number, Fr , a measure of the conditions at the surface of the liquid.

Rushton, Costich and Everett (42) have shown that for fully baffled systems the Froude number is insignificant. Further for Reynolds numbers corresponding to the turbulent region, ie Re greater than 10^4 , the power number is constant.

The restraining force was measured at varying stirrer speeds for both impellers using water at 25°C in the crystallizer and the power input of the stirrer calculated. The data are shown in Table 4.1 and are plotted on logarithmic co-ordinates in figs 4.1 and 4.2. Regression analyses show that the power required varied with the cube of the stirrer speed, the calculated exponents being 2.97 for the small impeller and 3.03 for the large impeller. The value of the power number for each impeller was 4.18 and 4.05 respectively, the calculations being shown at the foot of Table 4.1. These values are within the range 3 to 6 given by Rushton et. al. for six bladed turbine impellers in fully baffled vessels.

TABLE 4.1 POWER MEASUREMENTS

Speed (rps)	Restraining force (g)	Torque (g-cm)	Power input (W)	Re $\times 10^4$
4.98 cm diameter impeller, water at 25.0°C				
4.58	5	44.5	.126	1.136
6.83	10	88.9	.374	1.69
8.67	16	142	.759	2.15
9.83	20	178	1.078	2.44
10.67	24	213	1.400	2.65
12.2	31	276	2.08	3.03
13.8	40	356	3.03	3.42
14.5	45	400	3.57	3.60
15.3	50	444	4.19	3.79
16.3	55	489	4.91	4.04
16.8	60	533	5.52	4.17
17.3	65	578	6.16	4.29
18.1	70	622	6.94	4.49
18.7	75	667	7.69	4.64
19.2	80	711	8.42	4.76
19.8	85	756	9.23	4.91
20.4	90	800	10.06	5.06
21.0	95	844	10.93	5.21
21.6	100	889	11.84	5.36
22.2	105	933	12.76	5.51
22.9	110	978	13.80	5.68
23.3	115	1022	14.68	5.78
23.5	120	1067	15.5	5.83
24.7	130	1156	17.6	6.13
25.8	140	1245	19.8	6.40
26.7	150	1334	22.0	6.62
27.9	160	1422	24.4	6.92
29.2	170	1511	27.2	7.24

$$P = 0.001182 \text{ N}^3$$

$$N_p = \frac{0.001182}{0.0498^5 \times 10^{-3}} = 4.05$$

7.41 cm diameter impeller, water at 25.0°C

2.62	12	106.7	.173	1.44
3.00	15	134	.248	1.65
3.50	20	178	.384	1.92
3.88	25	222	.531	2.13
4.27	30	267	.702	2.35
4.53	35	311	.868	2.49
4.87	40	356	1.068	2.67
5.17	45	400	1.274	2.84
5.40	50	445	1.481	2.97
5.93	60	533	1.95	3.26
6.35	70	622	2.43	3.49
6.85	80	711	3.00	3.76
7.17	90	800	3.53	3.94
8.17	115	1022	5.15	4.49
9.33	153	1360	7.82	5.12
10.00	170	1510	9.31	5.49

$$P = 0.00933 \text{ N}^3$$

$$N_p = \frac{0.00933}{0.0741^5 \times 10^{-3}} = 4.18$$

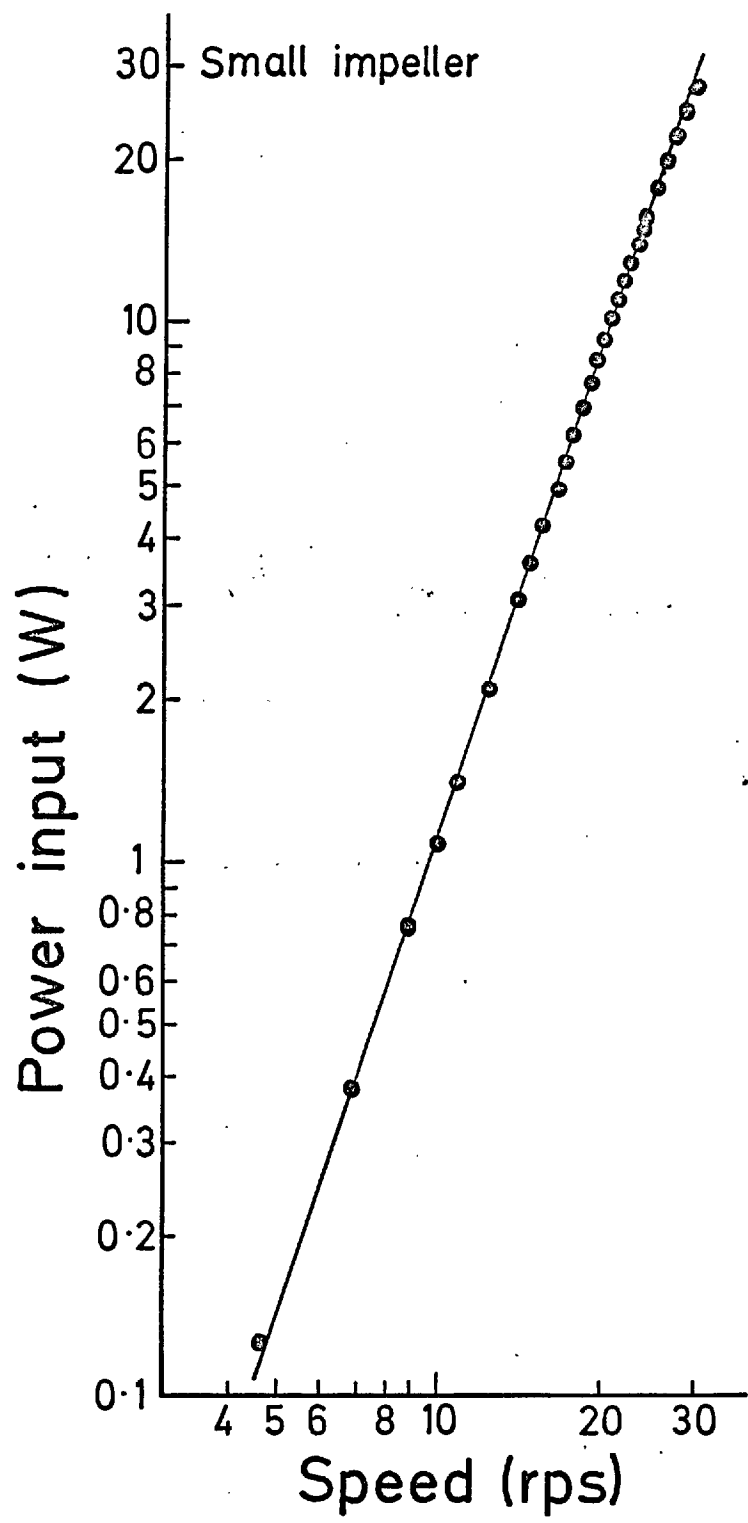


Fig 4.1

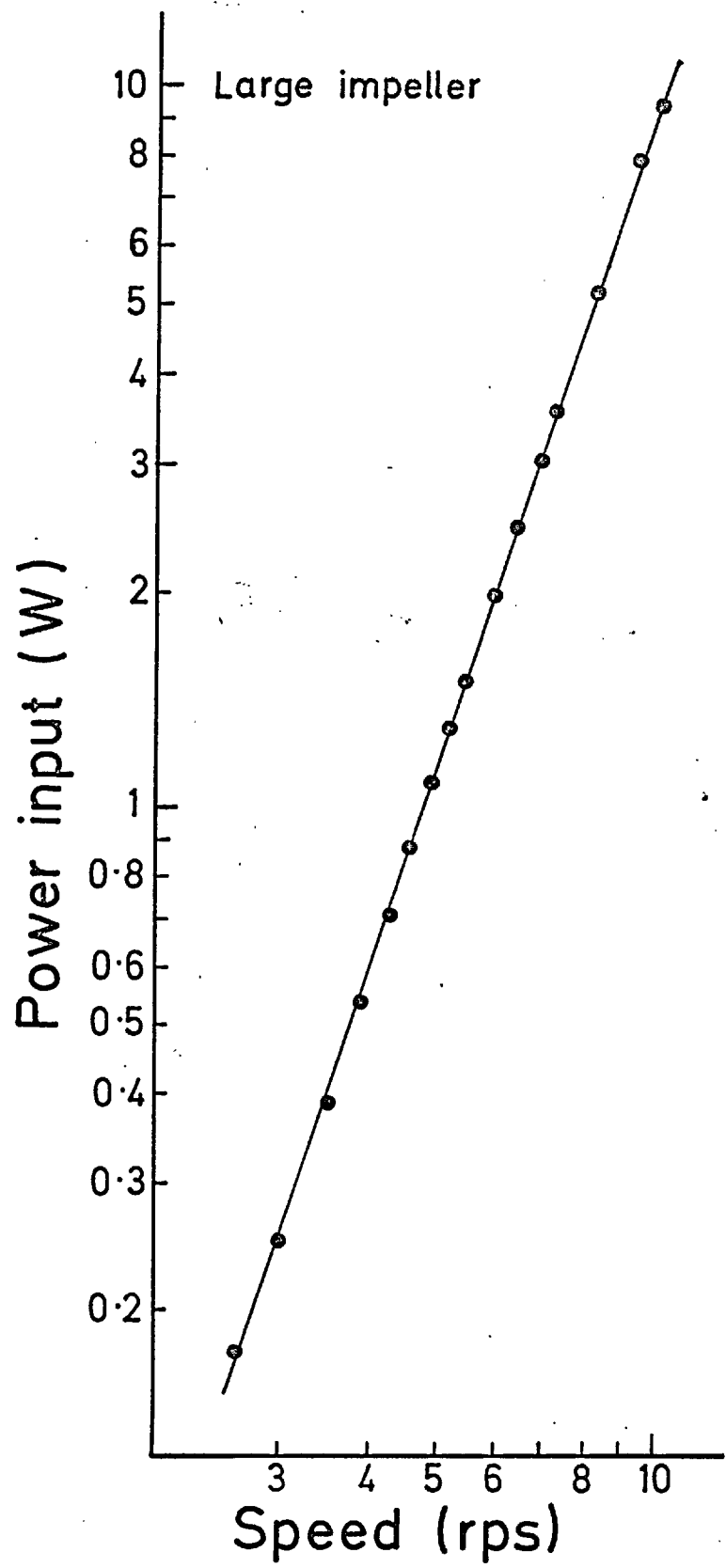


Fig 4.2

4.2 CRITERIA FOR ACCEPTING THE RESULTS OF A RUN

Before analysis of the results an attempt was made to ensure that the assumption, listed in Chapter 2, made in setting up the mathematical model were valid. The principal criterion used was that the size analyses of the product and suspended crystals were identical, thus checking that the crystallizer was operating under steady state conditions, and that there was no classification of the product crystals. Under conditions of low agitation the power input may be insufficient to keep all the crystals in suspension and the larger crystals will sink to the bottom of the crystallizer. At higher levels of agitation the feed rate selected may be such that either very high supersaturations would be found in the crystallizer, causing nucleation on the walls of the vessel and on the impeller, or that the supersaturation would be very low causing very little nucleation and very large crystals to be suspended. Runs were rejected when either the values of "L" for the product and suspended crystals differed by more than 10%, when there was visible evidence of crystals settling to the bottom or nucleation occurring on the walls or impeller. Examples of the size distributions obtained in these circumstances are shown in fig 4.3a, where there was visible settling of the crystals, the data points in the region 300-600 μm , and in fig 4.3b where the values of "L" differed by more than 10%.

In all 86 runs were performed and of these 33 were rejected, the values obtained for the runs which were accepted being shown in Table 4.2.

The full results for a run chosen at random are shown in Table 4.3 together with the calculations of the rates of growth and nucleation.

4.3 THE SIZE DISTRIBUTION

The results of the preliminary experiment described in Section 3.5 showed that the incomplete Gamma function gave the best description of

Fig 4.3a

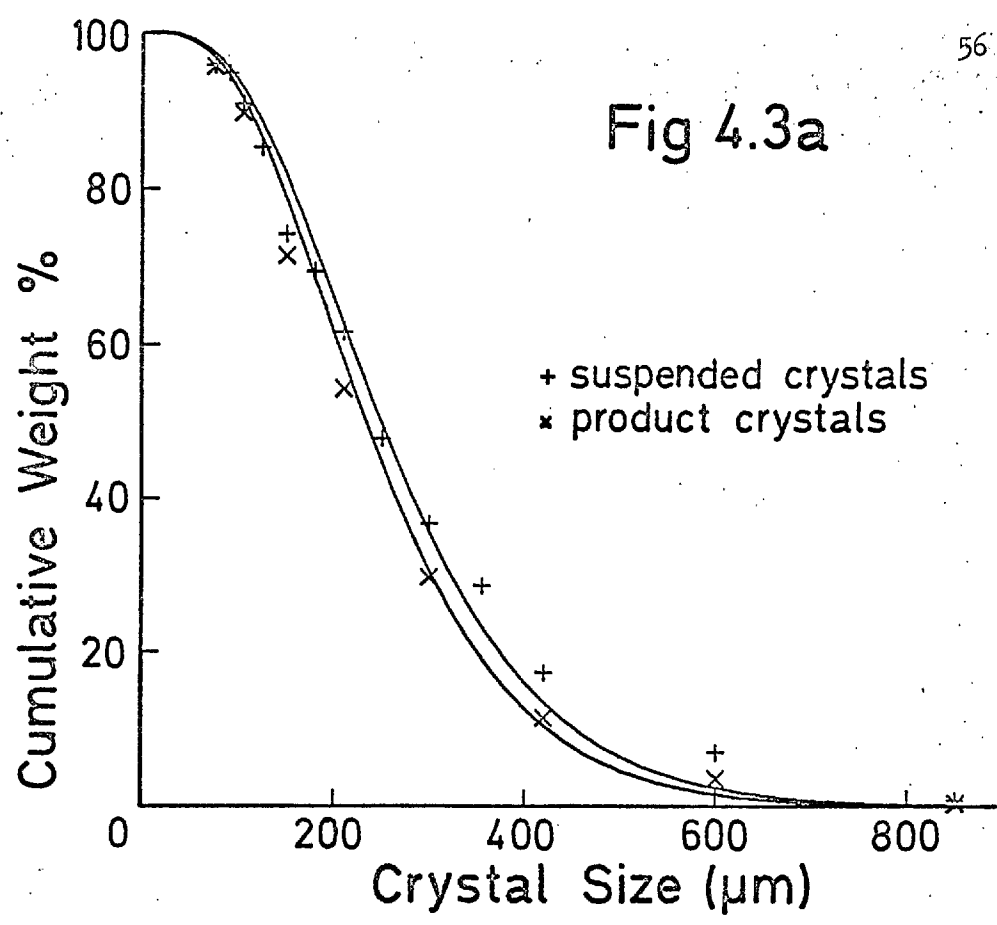
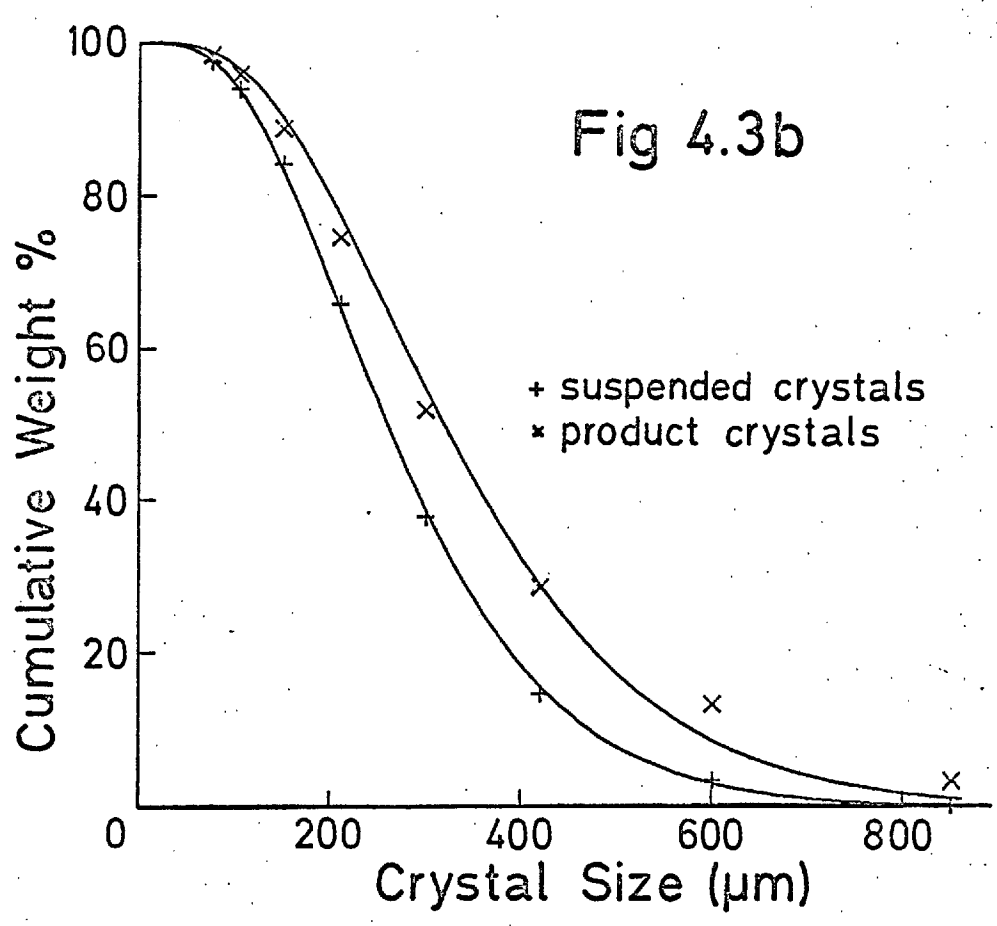


Fig 4.3b



<u>Feed</u>	<u>Solution</u>	<u>Jacket</u>
Flow Rate (ml/s)	Temp (°C)	Temp (°C)
6.49	33.5	26.0
8.53	32.5	24.5
9.21	32.0	24.5
4.33	32.5	24.5
8.88	31.6	24.5
6.71	31.8	24.5
4.36	32.5	24.5
6.49	30.2	24.5
11.05	34.0	24.6
7.33	32.6	25.0
11.88	34.3	25.0
5.27	33.0	25.0
12.52	34.1	20.7
8.17	32.5	25.2
4.17	32.7	25.0
13.76	30.5	25.0
13.56	32.4	25.0
1.52	34.9	25.0
10.16	32.6	25.0
7.09	32.4	24.5
12.65	33.4	25.0
7.45	32.4	25.0
7.00	32.4	25.0
12.84	34.8	25.0
5.55	33.9	25.0
3.24	35.5	20.6
13.62	33.5	20.8
3.41	26.6	20.7
10.37	28.8	26.7

TABLE 4.2 TABLE OF RESULTS

Run	F (g/s)	Temp (°C)	W (g)	S (%)	L (μm)	n	k _t (μm/s)	N _O (10 ³ /s)
7.41 cm diameter impeller, 750 rpm 18.2 W power input								
22/6	0.0530	31.1	18.63	0.85	61.1	-0.126	0.174	20.6
24/6	0.0557	30.5	15.65	0.87	58.1	-0.164	0.207	25.1
25/6	0.0361	30.6	10.52	0.92	59.0	-0.029	0.202	15.6
26/6	0.0470	29.7	23.78	0.63	63.1	-0.287	0.125	16.5
29/6	0.0494	29.7	12.22	1.08	58.1	-0.099	0.235	22.3
30/6	0.0439	29.9	15.6	0.71	56.5	-0.064	0.159	21.6
1/7	0.0513	29.5	23.17	0.71	60.8	-0.211	0.135	20.2
3/7	0.0331	28.7	11.72	0.73	61.2	-0.112	0.174	12.8
8/7	0.0639	32.0	14.07	1.16	56.8	-0.035	0.258	30.8
21/9	0.0506	30.5	14.85	0.88	57.1	-0.129	0.195	24.0
30/9	0.0832	32.0	15.76	1.25	56.5	-0.006	0.298	40.8
12/10	0.0564	30.2	21.01	0.68	52.9	-0.079	0.142	33.6
7.41 cm diameter impeller, 600 rpm 9.3 W power input								
17/11	0.0697	31.9	12.13	1.69	50.5	0.099	0.290	47.8
18/11	0.0561	30.2	13.48	1.30	55.6	-0.085	0.231	28.8
19/11	0.0516	29.5	23.26	0.81	55.0	-0.113	0.122	27.4
23/11	0.0082	29.6	1.99	1.34	54.6	0.067	0.224	4.4
24/11	0.0416	30.7	6.77	1.83	54.7	-0.059	0.336	22.5
26/11	0.0371	29.2	43.03	0.35	65.7	-0.275	0.057	11.6
30/11	0.0453	30.7	9.14	1.50	53.2	-0.066	0.283	26.6
7.41 cm diameter impeller, 500 rpm 5.4 W power input								
17/6	0.0595	29.8	19.57	1.31	64.2	-0.129	0.195	19.8
19/8	0.0264	31.9	6.46	1.77	60.2	0.169	0.246	10.7
23/9	0.0183	31.1	5.71	1.33	63.6	-0.028	0.204	6.3
28/9	0.0194	31.1	6.91	1.15	63.2	0.004	0.178	6.8
6/10	0.0705	32.2	12.25	2.29	58.3	0.055	0.335	31.5
7/10	0.0658	30.5	26.08	1.17	64.9	-0.023	0.164	21.3
19/10	0.1214	26.7	82.52	0.63	70.2	-0.057	0.103	31.0
21/10	0.0504	31.6	9.95	1.94	54.2	0.074	0.275	27.9
22/10	0.0068	25.8	4.54	0.71	68.6	-0.008	0.103	1.9
23/10	0.0095	27.8	2.66	1.53	58.7	-0.126	0.211	4.2

<u>Feed</u>	<u>Solution</u>	<u>Jacket</u>
Flow Rate	Temp	Temp
(ml/s)	(°C)	(°C)
8.77	31.9	25.0
5.56	31.5	25.0
3.85	30.6	25.1
4.85	33.0	27.1
7.51	31.9	27.0
4.55	31.4	27.0
13.42	31.0	27.0
5.91	35.1	20.9
8.08	35.9	20.9
11.70	36.1	20.9
12.20	34.8	20.9
8.74	32.7	25.0
3.87	34.0	25.0
4.20	37.0	20.6
6.92	35.5	25.0
13.06	32.5	25.0
12.80	32.5	25.0
12.20	33.9	25.0
6.22	33.6	25.0
4.58	33.5	25.0
12.57	33.4	25.0
6.36	33.4	25.0
3.70	33.0	25.0
11.90	33.4	25.2

TABLE 4.3 RESULTS FROM A TYPICAL RUN

Run 17/11; 7.41 cm diameter impeller, 600 rpm

Crystal size distributions:-

Size (μm)	Suspended crystals		Product crystals	
	wt retained (g)	% retained	wt retained (g)	% retained
850	0.0026	0.021		
710	0.0096	0.079		
600	0.0355	0.293	0.0013	0.120
500	0.1392	1.148		
420	0.3605	2.972	0.0290	2.69
355	0.8970	7.395		
300	1.8427	15.191	0.1581	14.64
250	3.0550	25.185		
210	4.7821	39.423	0.4214	39.02
180	6.7186	55.388		
150	7.6194	62.814	0.6888	63.78
125	9.0281	74.427		
105	10.1302	83.513	0.9122	84.47
90	10.9444	90.225		
75	11.1298	91.754	1.0048	93.05
	12.1301		1.0799	

Product crystals collected in 15.5 secs,
ie rate of production = $1.0799/15.5$

$$= 0.0697 \text{ g/s}$$

Operating temperature of crystallizer

$$= 31.9^\circ\text{C}$$

Temperature of feed solution

$$= 34.9^\circ\text{C}$$

Temperature of cooling jacket

$$= 25.2^\circ\text{C}$$

Concentration of solution

$$= 22.891 \text{ g/100 g solution}$$

Saturation concentration at 31.9°C

$$= 22.510 \text{ g/100 g solution}$$

Supersaturation

$$= 1.69\%$$

From the size distribution of the suspended
crystals, $L = 50.5 \mu\text{m}$

$$\text{Growth rate} = L \cdot F/W = 50.5 \times 0.0697/12.13 = 0.290 \mu\text{m/s}$$

$$\begin{aligned} \text{Nucleation rate} &= F/(6 \times \rho L^3) = \frac{0.0697}{6 \times 0.966 \times 1.952 \times 50.5^3} \times 10^{12} \\ &= 47.8 \times 10^3 \text{ s}^{-1} \end{aligned}$$

the size distribution obtained experimentally. The agreement between the size distributions of the product and suspended crystals is shown in fig 4.4 which gives the results for the run selected at random. When compared with fig 4.3 it shows that it was easy to distinguish between an acceptable run and one which ought to be rejected.

4.4 THE VALUE OF "n"

The mean value of "n", the exponent of crystal size in the growth rate equation, was -0.026 with a standard deviation of 0.097. For 52 degrees of freedom the mean value of -0.026 is insignificantly different from zero by Student's t test and therefore the rate of growth of a freely suspended crystal of ammonium perchlorate is independent of its size.

A value of zero for "n" was used when calculating the rates of growth and nucleation shown in Table 4.2.

The zero value of "n" has been assumed by a number of workers, Saeman (45), Robinson & Roberts (41), Randolph (38), who have then shown that the experimental size distribution agreed well with the theory. The technique of calculating the value of "n" from the experimental data is a novel one.

4.5 THE RATE OF GROWTH

The values of the rate of growth shown in Table 4.2 for the larger impeller are shown graphically in fig 4.5 for the various impeller speeds, the lines being drawn by the method of least squares. This shows that the rate of growth of ammonium perchlorate is linear with supersaturation over the range investigated and increases with increasing impeller speed. The specific rates of growth, ie the growth rate at 1% supersaturation given by the slope of the lines in fig 4.5, are plotted against the impeller speed using logarithmic co-ordinates in fig 4.6. This shows that the rate of growth is proportional to the power 0.78 of the impeller speed.

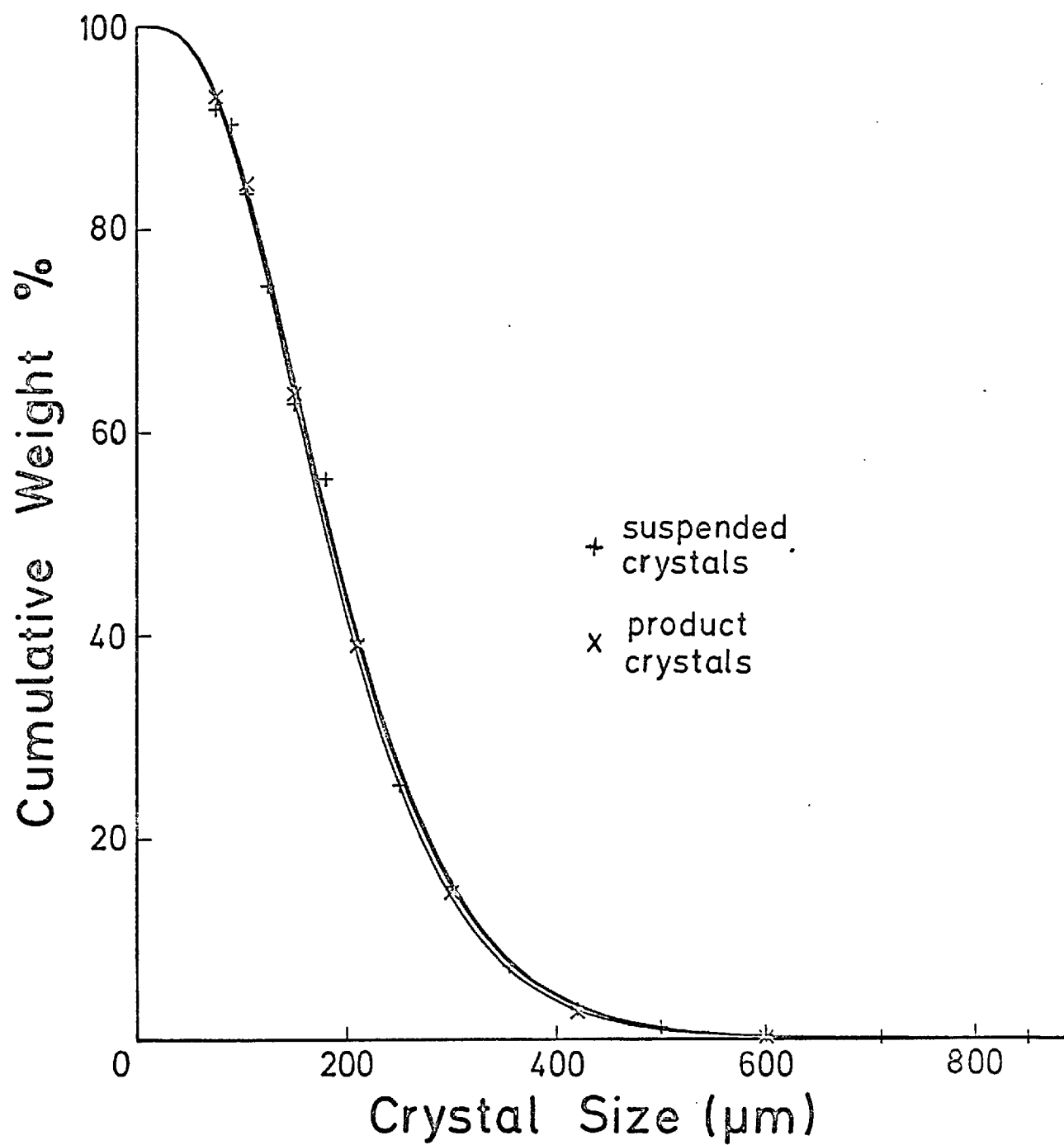


Fig4.4 Typical Size Distribution

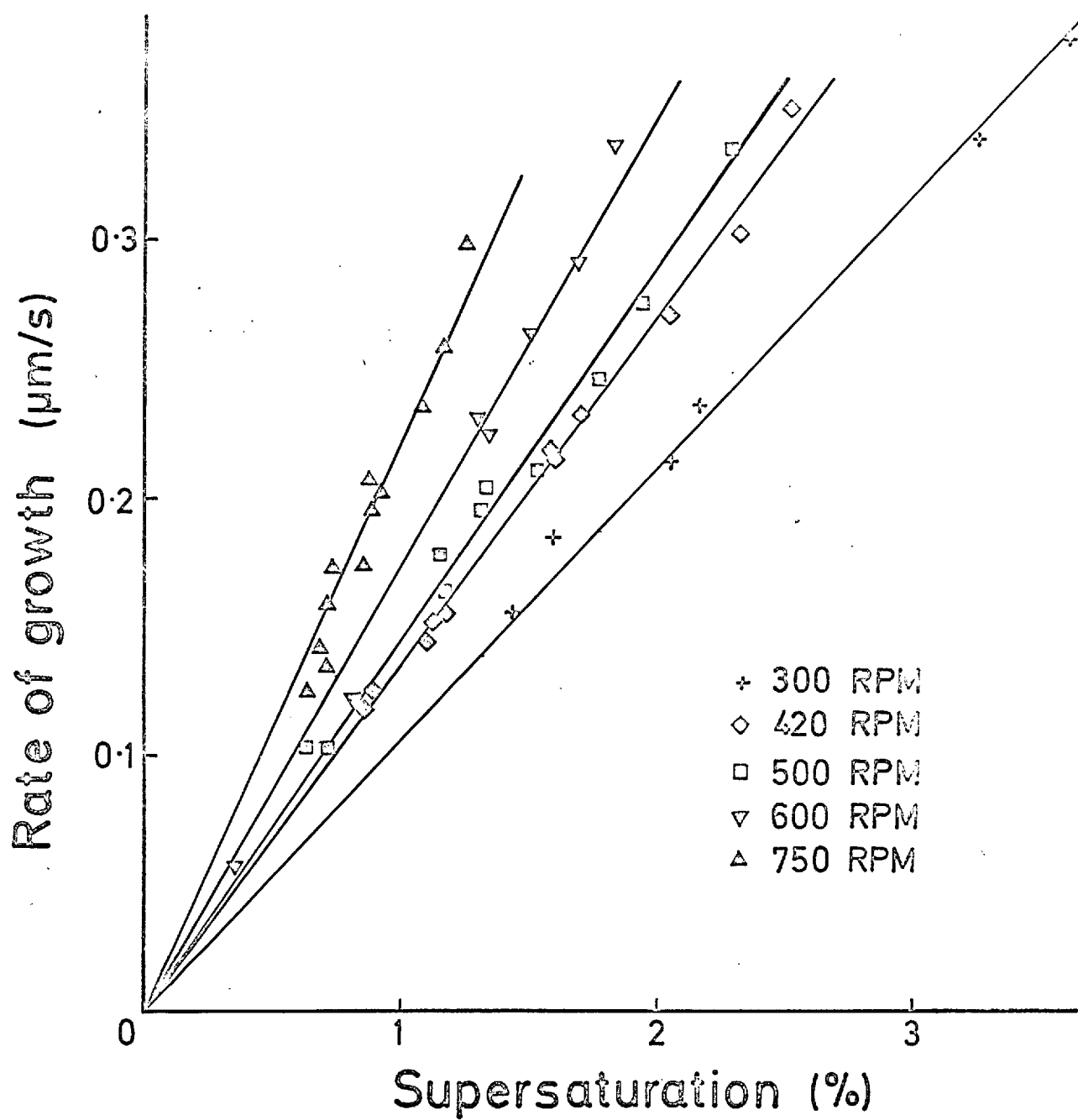


Fig 4.5

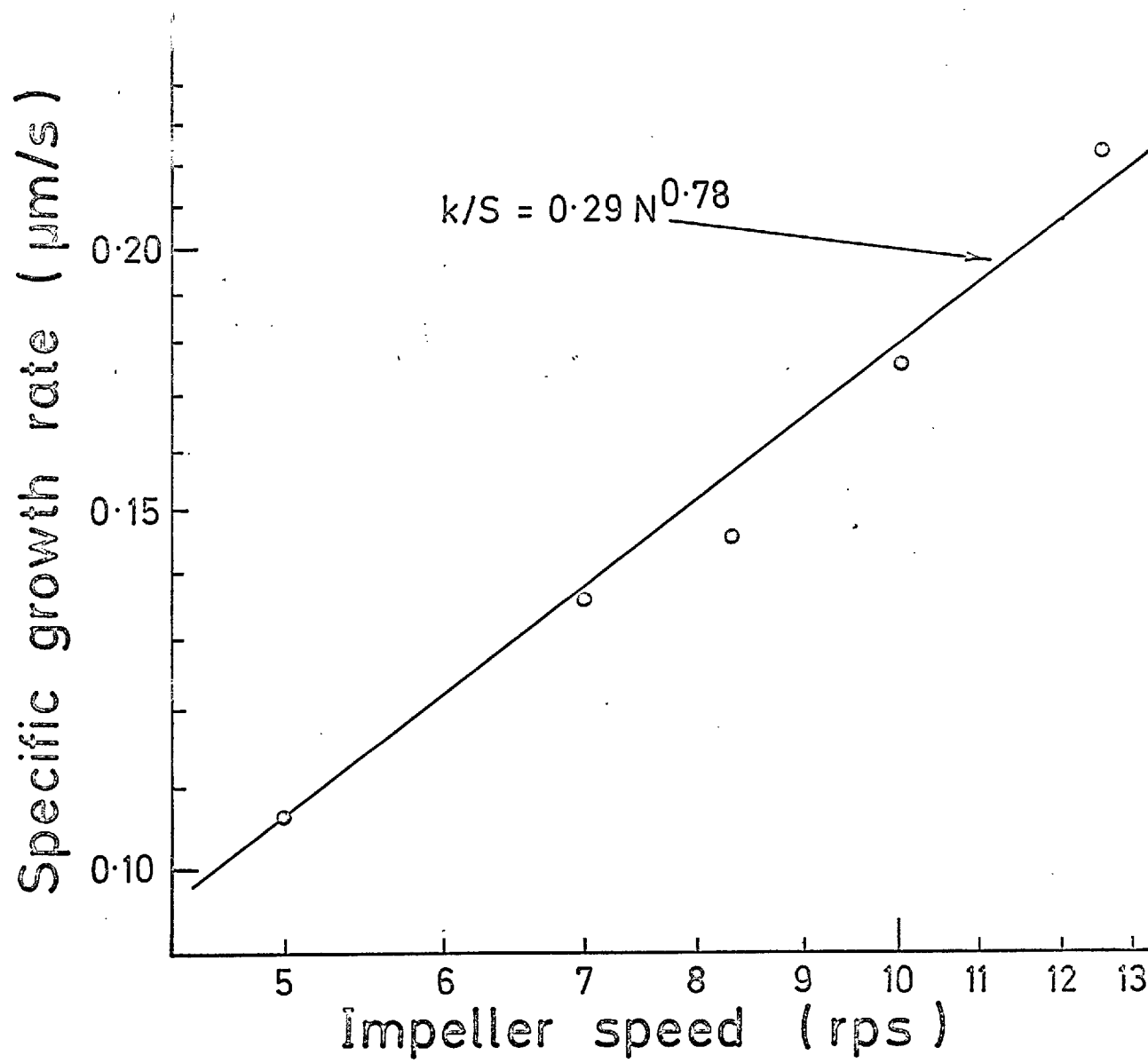


Fig 4.6

If the rate of growth is controlled by the diffusion through the boundary layer, Bransom, Brown and Watts (9) showed that the rate of growth will be proportional to the fourth root of the power input per unit volume of the system, and this explained their results on the rate of growth of magnesium sulphate heptahydrate. The power input to the system has been shown to be proportional to the cube of the impeller speed in Section 4.1 so that the dependence shown in fig 4.6 is equivalent to a dependence on power input raised to the power 0.26, and this is in very good agreement with the exponent 0.25 found by Bransom, Brown and Watts.

That the power input to the system is the correct dependence is shown in fig 4.7 where the rate of growth divided by the fourth root of the power input is plotted against the supersaturation for all the experimental data. The results obtained using the large and small impellers fall on the same straight line, the conclusion being that the rate of growth of freely suspended crystals of ammonium perchlorate is linear with supersaturation and proportional to the fourth root of the power input to the crystallizing system.

4.6 THE RATE OF NUCLEATION

The rate of nucleation was calculated by substituting the experimental values into equation 2.14, the values being shown in Table 4.2. There is no clear correlation between the rate of nucleation and the supersaturation. As the weight and therefore number of crystals in suspension varied with each run it is likely that the rate of nucleation is dependent on some property of the suspended crystals. Table 4.4 shows the rate of nucleation and the properties of the suspended crystals. While there is some correlation between the rate of nucleation and the number of crystals, a better correlation is obtained between the nucleation rate and the area of the crystals, the values being plotted in figs 4.8 to 4.12. The lines

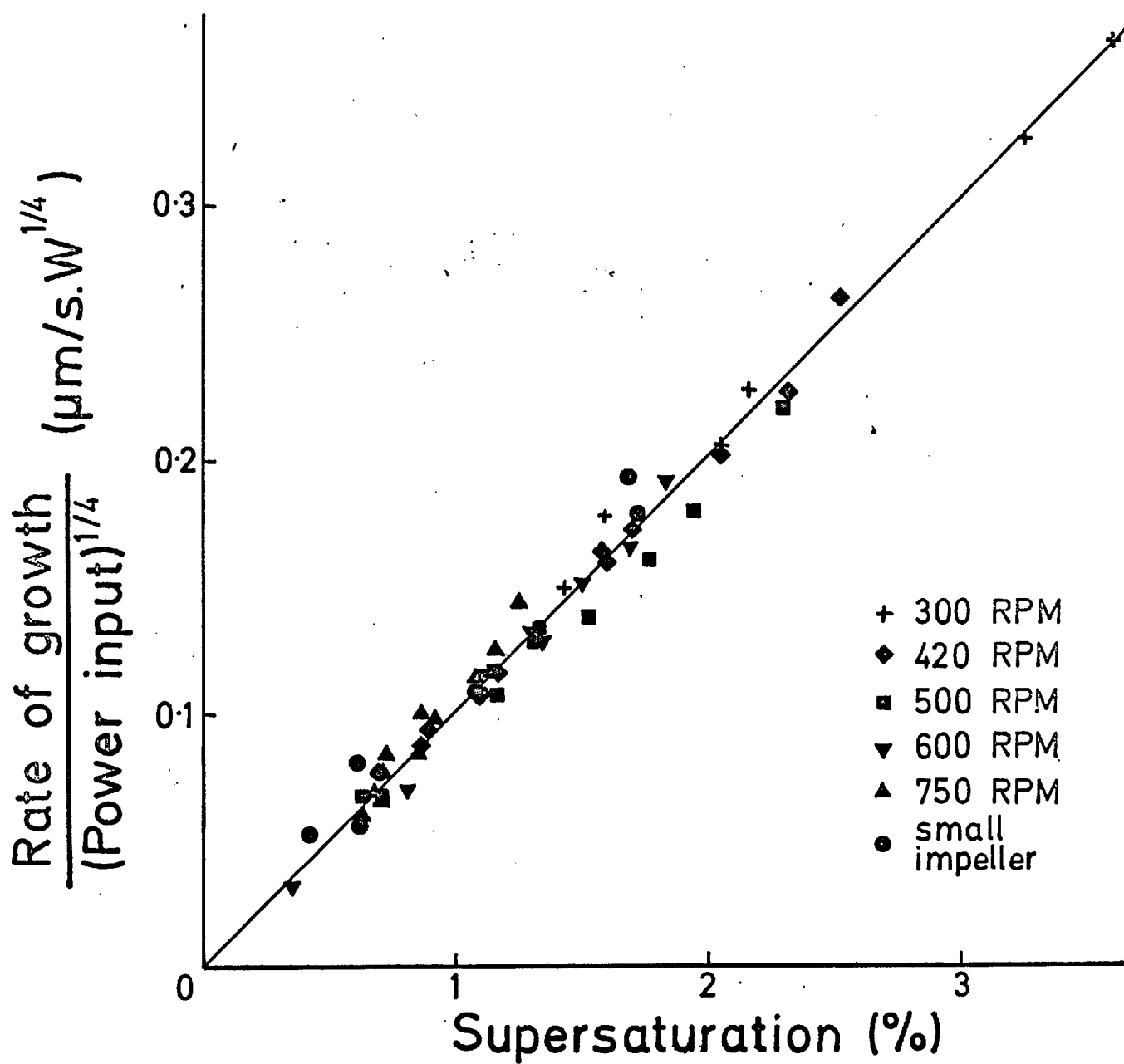


Fig 4.7

TABLE 4.4 PROPERTIES OF THE SUSPENDED CRYSTALS

Run	N_0 ($10^3/s$)	S (%)	N' (10^6)	A (m^2)	W (g)	N_0/A ($s^{-1}cm^{-2}$)	$(N_0/A)/(N'^2D)$ (s/cm^3)
7.41 cm diameter impeller, 750 rpm 18.2 W power input							
22/6	20.6	0.85	7.23	0.960	18.63	2.14	0.00185
24/6	25.1	0.87	7.07	0.848	15.65	2.97	0.00257
25/6	15.6	0.92	4.54	0.562	10.52	2.77	0.00239
26/6	16.5	0.63	8.35	1.185	23.78	1.39	0.00120
29/6	22.3	1.08	5.51	0.662	12.22	3.36	0.00290
30/6	21.6	0.71	7.67	0.870	15.62	2.48	0.00214
1/7	20.2	0.71	9.13	1.200	23.17	1.69	0.00146
3/7	12.8	0.73	4.53	0.603	11.72	2.12	0.00183
8/7	30.8	1.16	6.77	0.779	14.07	3.95	0.00341
21/9	24.0	0.88	7.03	0.818	14.85	2.93	0.00253
30/9	40.8	1.25	7.72	0.877	15.76	4.65	0.00402
12/10	33.6	0.68	12.52	1.249	21.01	2.69	0.00232
7.41 cm diameter impeller, 600 rpm 9.3 W power input							
17/11	47.8	1.69	8.32	0.756	12.13	6.33	0.00854
18/11	28.8	1.30	6.92	0.762	13.48	3.78	0.00510
19/11	27.4	0.81	12.35	1.330	23.26	2.06	0.00278
23/11	4.4	1.34	1.08	0.115	1.99	3.86	0.00521
24/11	22.5	1.83	3.66	0.390	6.77	5.77	0.00779
26/11	11.6	0.35	13.44	2.062	43.03	0.56	0.00076
30/11	26.6	1.50	5.37	0.541	9.14	4.92	0.00664
7.41 cm diameter impeller, 500 rpm 5.4 W power input							
17/6	19.8	1.31	6.53	0.958	19.57	2.07	0.00402
19/8	10.7	1.77	2.61	0.338	6.46	3.16	0.00614
23/9	6.3	1.33	1.96	0.282	5.71	2.22	0.00431
28/9	6.8	1.15	2.42	0.344	6.91	1.98	0.00385
6/10	31.5	2.29	5.48	0.662	12.25	4.76	0.00925
9/10	21.3	1.17	8.44	1.265	26.08	1.69	0.00328
19/10	31.0	0.63	21.05	3.696	82.52	0.84	0.00163
21/10	27.9	1.94	5.51	0.577	9.95	4.84	0.00941
22/10	1.9	0.71	1.24	0.208	4.94	0.89	0.00173
23/10	4.2	1.53	1.16	0.142	2.66	2.93	0.00569

TABLE 4.4 PROPERTIES OF THE SUSPENDED CRYSTALS (continued)

Run	N_0 ($10^3/s$)	S (%)	N' (10^6)	A (m^2)	W (g)	N_0/A ($s^{-1}cm^{-2}$)	$(N_0/A)/(N'^2D)$ (s/cm^3)
7.41 cm diameter impeller, 420 rpm 3.2 W power input							
1/12	13.6	1.70	3.76	0.544	11.04	2.50	0.00689
2/12	10.9	1.12	4.86	0.794	17.10	1.38	0.00380
3/12	9.1	0.86	5.49	1.002	22.82	0.90	0.00248
4/12	16.3	1.10	7.78	1.297	28.20	1.26	0.00347
7/12	9.7	1.58	2.92	0.456	9.59	2.12	0.00584
8/12	6.4	0.89	3.59	0.651	14.76	0.98	0.00270
9/12	6.7	2.52	1.21	0.171	3.43	3.93	0.01082
10/12	32.8	1.17	14.75	2.528	55.79	1.30	0.00358
11/12	47.5	1.60	13.77	1.899	37.56	2.50	0.00689
14/12	21.8	2.05	4.78	0.592	11.12	3.68	0.01014
15/12	45.7	2.32	8.85	1.078	20.04	4.24	0.01168
7.41 cm diameter impeller, 300 rpm 1.2 W power input							
29/4	12.7	1.59	5.68	1.399	36.99	0.90	0.00486
1/5	10.3	1.43	5.37	1.248	32.07	0.83	0.00448
7/5	14.4	2.05	5.37	1.215	30.77	1.19	0.00642
8/8	17.9	2.16	5.94	1.302	32.46	1.37	0.00740
14/10	9.1	3.25	1.86	0.316	6.93	2.89	0.01560
9/11	4.5	3.60	0.78	0.123	2.59	3.65	0.01970
4.98 cm diameter impeller, 1200 rpm 9.5 W power input							
25/8	77.6	1.07	16.46	0.965	12.44	8.05	0.00404
26/8	33.5	0.70	13.20	1.349	22.97	2.48	0.00124
27/8	30.0	0.62	16.45	1.710	29.36	1.75	0.00088
4.98 cm diameter impeller, 1000 rpm 5.5 W power input							
1/9	25.7	1.72	4.13	0.285	3.99	9.01	0.00651
3/9	34.3	0.61	14.97	1.570	27.09	2.19	0.00158
4/9	19.5	0.42	14.71	1.961	38.16	0.99	0.00072
4.98 cm diameter impeller, 800 rpm 2.8 W power input							
9/9	13.8	1.68	3.13	0.356	6.40	3.88	0.00438

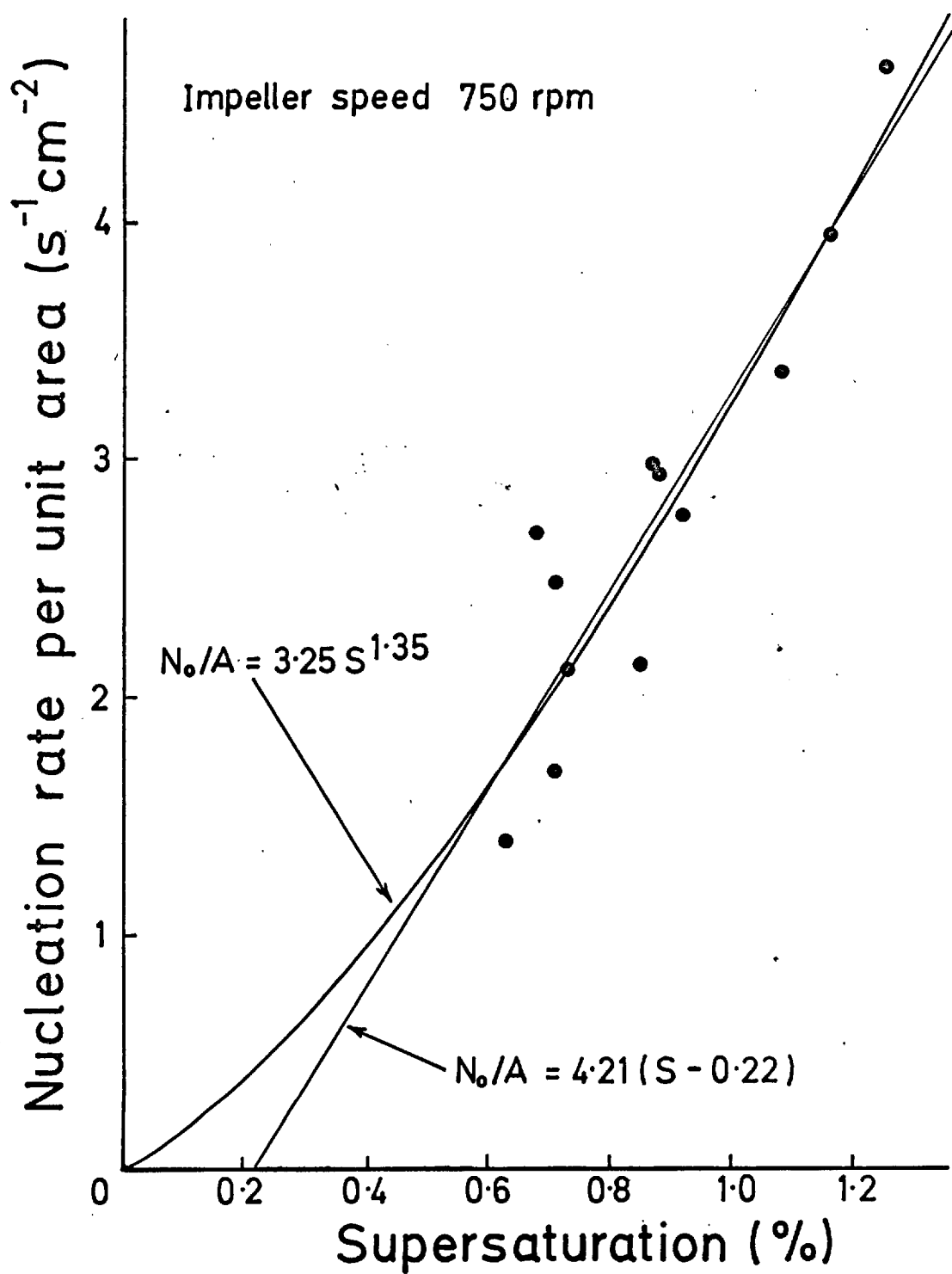


Fig 4.8

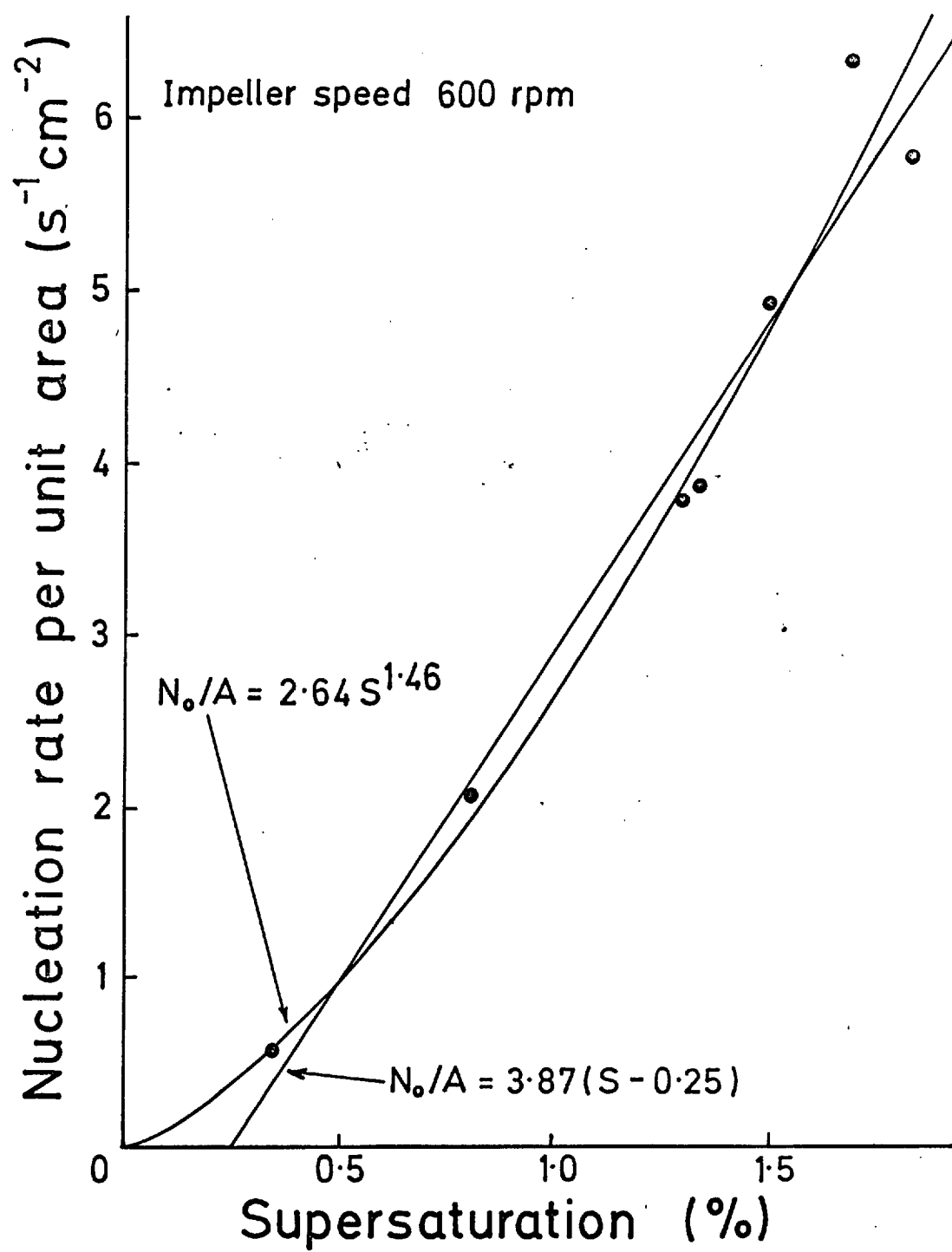


Fig 4.9

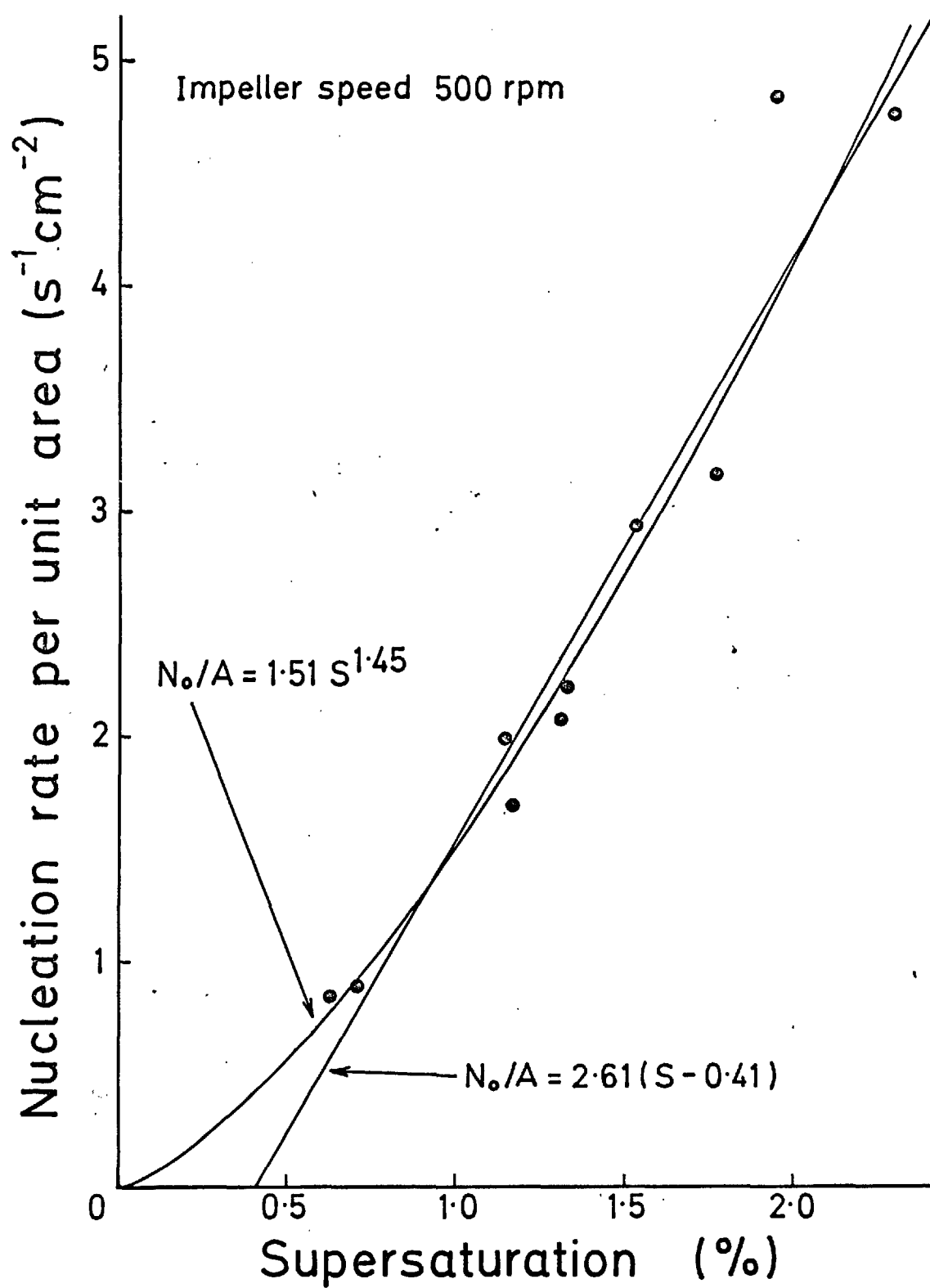


Fig 4.10

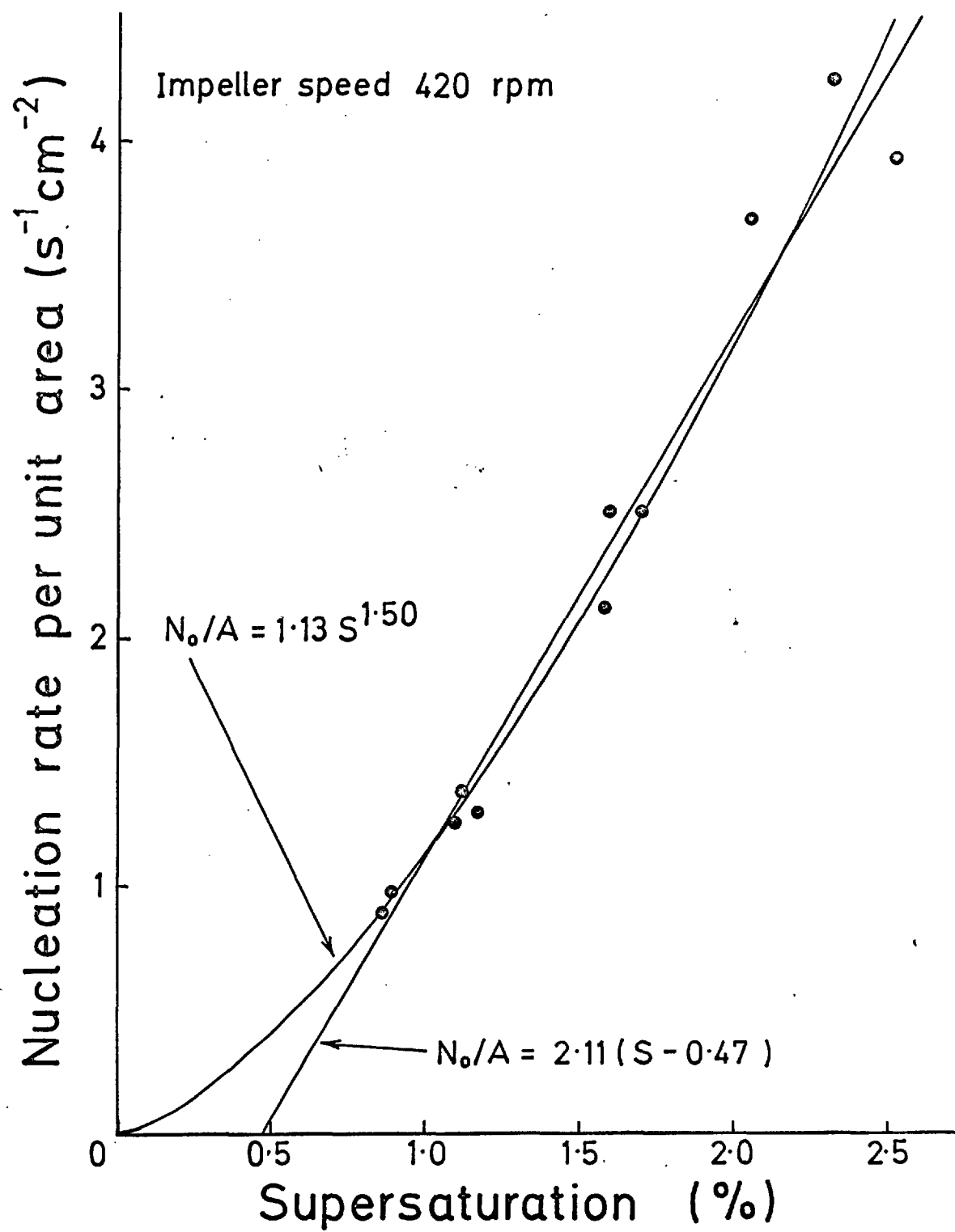


Fig 4.11

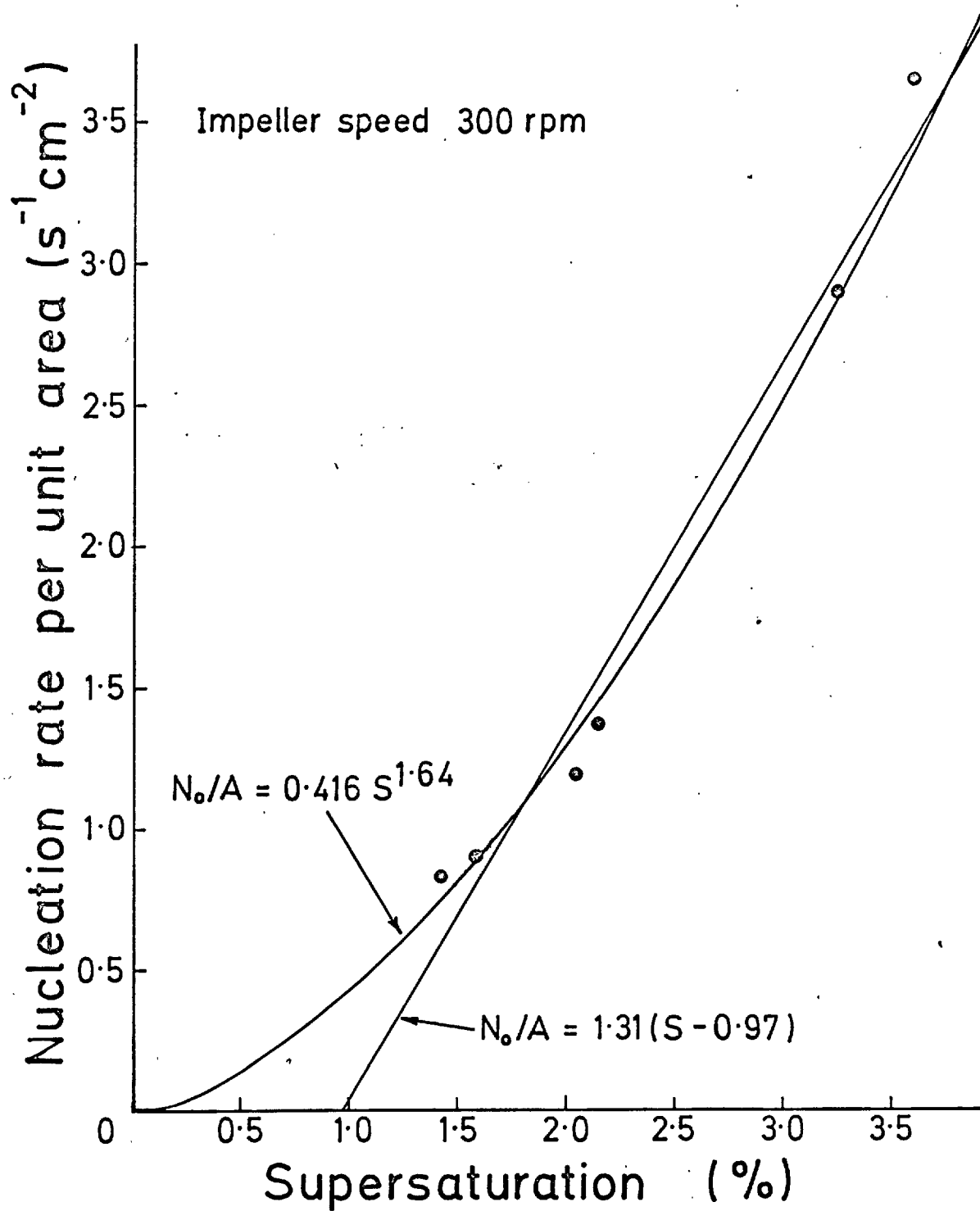


Fig 4.12

drawn are the least squares fits assuming the relationship to be either a power law with supersaturation or linear with supersaturation there being insufficient data or too much experimental error to indicate which relationship is the true one.

Figs 4.8 to 4.12 show that the rate of nucleation per unit area of suspended crystal increases with increasing stirrer speed. A minimisation analysis showed that the rate was proportional to the square of the speed. When this term was used with the results obtained with the smaller impeller it was found that these could be also correlated by using the term $(\text{impeller speed})^2 \times \text{impeller diameter}$. The rates of nucleation in Table 4.2 have been divided by this factor and are shown in Table 4.4 and plotted against supersaturation in fig 4.13, the curve being drawn by the method of least squares. Fig 4.13 shows that the rate of nucleation is a power law with supersaturation being given by the expression:

$$N_0 = 0.00293 S^{1.48} \times A \times N^2 \times D$$

4.7 SUMMARY OF RESULTS

It has been shown that:

- 1) The power input of a turbine impeller is proportional to the cube of the impeller speed;
- 2) The size distribution of the crystals produced by a continuous crystallizer operating under steady state conditions is best described by the incomplete Gamma function;
- 3) The rate of growth of ammonium perchlorate crystals is
 - a) linear with supersaturation,
 - b) independent of the crystal size,
 - c) proportional to the fourth root of the power input to the crystallizer;

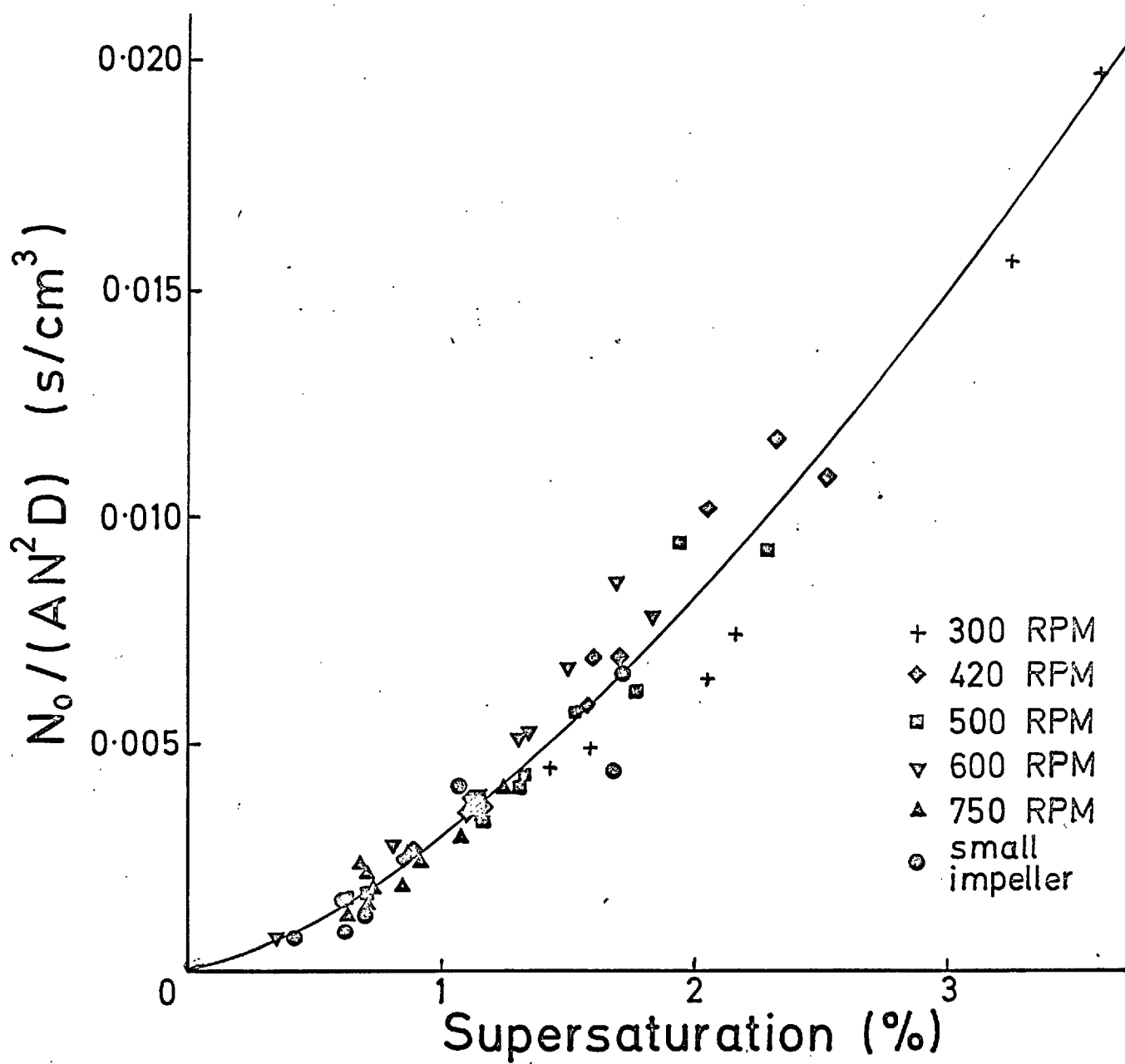


Fig 4.13

- 4) The rate of nucleation is proportional to the surface area of the crystals suspended in the crystallizer;
- 5) The rate of nucleation per unit area of suspended crystal is
 - a) a power law dependence on supersaturation with an exponent of 1.48,
 - b) proportional to the square of the impeller speed and the impeller diameter.

CHAPTER 5 DISCUSSION OF THE RESULTS

5.1	INTRODUCTION	77
5.2	THE EFFECT OF SUPERSATURATION	78
5.3	THE TYPES OF COLLISION	80
	Crystal-Crystal Collisions	82
	Crystal-Vessel Collisions	82
	Crystal-Impeller Collisions	83
5.4	THE EFFECT OF CRYSTAL SURFACE AREA	85
5.5	APPLICATION OF THE RESULTS TO LARGE SCALE CRYSTALLIZERS	87
	Example 1	87
	Example 2	89
5.6	SUMMARY AND CONCLUSIONS	91

5.1 INTRODUCTION

The results of the previous chapter show that appreciable nucleation takes place in an agitated bed of crystals even at low supersaturations and it seems likely that the majority of the nucleation is produced by collision breeding of the crystals. Two topics will be discussed, covering broadly the nature of the crystal collisions and the way in which nuclei are formed after a collision has taken place.

The collisions may be of three types; 1) crystal-crystal collisions, 2) crystal-vessel collisions, 3) crystal-impeller collisions. Clontz and McCabe (15) reported that edge contacts and sliding contacts at low angles of approach to the crystal produced more nuclei than contacts normal to the crystal face. In an agitated bed of crystals the angle and orientation of the crystals before a collision will be randomly distributed throughout the crystal bed and will therefore appear in any equation for the overall rate of nucleation as a statistical mean.

Before a collision can take place the laminar layer of solution surrounding the crystal will have to be displaced. Clontz and McCabe found no threshold value of impact energy before any nuclei were produced, the conclusion being that either the displacement of the laminar layer has little effect on the formation of nuclei after a collision, or that the nuclei are produced by or during the displacement of the laminar layer.

Two possible ways in which collision breeding could occur are 1) mechanical breakage of the crystal at the point of impact to produce crystal fragments, 2) nucleation in the surface layer surrounding the crystal. Mechanism 1) is self explanatory. For mechanism 2) the

solute molecules in the vicinity of the growing crystal will have to have some degree of "ordering" to form what may be called quasi-crystalline structures so that when they are removed from the vicinity of the crystal surface they form stable nuclei. This "ordering" may be a direct result of the collision of a crystal or there may be some degree of "order" of solute molecules in a supersaturated solution. Mullin and Leci (32) have observed concentration gradients in a supposedly homogeneous supersaturated aqueous solution of citric acid consistent with the formation of molecular clusters of the solute. Lal, Mason and Strickland-Constable (20) and Clontz and McCabe (15) have shown that if the clusters exist for magnesium sulphate heptahydrate, then they cannot be removed by fluid shear alone, as was suggested by Powers (37). However the more positive mechanical forces involved in a crystal collision may do so.

5.2 THE EFFECT OF SUPERSATURATION

The two mechanisms for nucleus formation differ greatly when the effect of supersaturation is considered.

MECHANISM 1)

It is difficult to see why the tendency for a crystal to fracture after a collision should depend on supersaturation. Lal, Mason and Strickland-Constable therefore made a further assumption that the crystal fragments resulting from a collision were of the same order of size as the critical nucleus at the given supersaturation, as given by the Gibbs-Thomson equation;

$$r_c = \frac{2\sigma v}{RT \ln (c/c_0)} \quad 1.1$$

As the concentration ratio c/c_0 is low this equation becomes

$$r_c = \frac{2\sigma v}{RTS} \quad 5.1$$

where σ is the interfacial Gibbs free energy and v the molecular volume, R the gas constant, T the absolute temperature and S the supersaturation. At low supersaturations the critical size r_c , will be large and most of the fragments will redissolve. At higher supersaturations the critical size will be smaller and a greater proportion of the fragments will survive.

MECHANISM 2)

If quasi-crystalline clusters are formed around a growing crystal then the size of the clusters or the number of clusters, or both, would increase with increasing supersaturation and the number of nuclei produced after a collision would increase accordingly. At very high supersaturations in the absence of any crystal collisions these clusters could possibly enter into the growth process of the crystal, and indeed needle growth of magnesium sulphate heptahydrate at high supersaturations has been observed by both Lal, Mason and Strickland-Constable (20) and Clontz and McCabe (15) in connection with needle breeding.

The dependence of the nucleation rate on supersaturation is shown in fig 4.13 as a power law, with an exponent of supersaturation of 1.48. This differs from the conclusions drawn by Bransom, Brown and Heeley (8), using a similar experimental technique, who showed a linear relationship with supersaturation after a threshold value had been exceeded, similar to the straight lines shown in figs 4.8 to 4.12. However a power law relationship would describe their results equally well, the exponent of supersaturation being in the range 1.7 to 2.0.

Lal, Mason and Strickland-Constable (20) obtained an "S" shaped curve for the dependence on supersaturation. The results of this work, with a much lower range of supersaturation agree qualitatively with

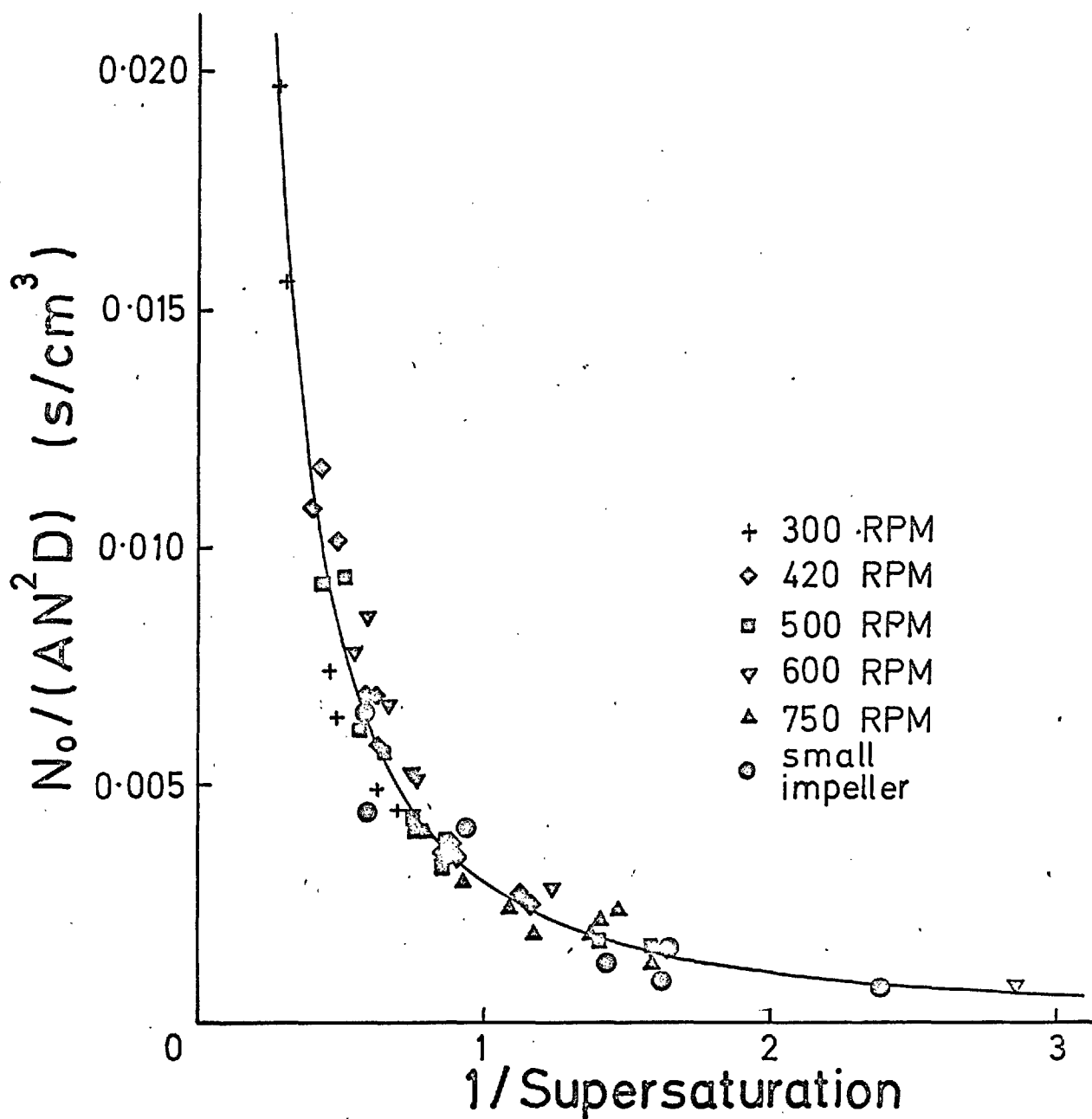
the lower portion of this "S" shaped curve. It is not suggested that the power law dependence on supersaturation is a "natural" law, but rather a sufficient description of the results obtained over the range of supersaturation investigated.

If the nucleation were caused by mechanism 1), applying the assumption that the particles so produced are of the same order of size as the critical nucleus, the power law dependence of nucleation with supersaturation results in an hyperbolic-type size distribution of the crystal fragments. In fig 5.1 the nucleation rate from fig 4.13 is plotted against the reciprocal of the supersaturation, which from the Gibbs-Thomson equation (equation 5.1) is equivalent to a scale of the size of the critical nucleus. The nucleation rate is then proportional to the number of fragments having a size larger than the critical nucleus.

The derivative of the curve in fig 5.1 would then be the number of fragments produced of a given size per unit time and will be of a similar hyperbolic-type shape as fig 5.1. The curve of fig 5.1 is in marked contrast to the straight line dependence obtained by Lal, Mason and Strickland-Constable (20) using a much larger range of supersaturation.

5.3 THE TYPES OF COLLISIONS

In the three types of collision described the rate of nucleation will be the product of the number of nuclei produced by a single collision and the frequency of that collision in the agitated bed of crystals. Clontz and McCabe (15) showed that the number of nuclei produced by a collision was proportional to the impact energy per unit area of collision surface. If the energy of impact of a crystal is the



Scale linear with r_c (Arbitrary Units)

Fig 5.1

change in kinetic energy of the crystal on collision, this will be given by:

$$\begin{aligned}\text{energy} &= \frac{1}{2} m v_r^2 \\ &= \frac{1}{2} \alpha \rho l^3 v_r^2\end{aligned}\quad 5.2$$

where m is the mass of the crystal and v_r the change in the velocity of the crystal. In the absence of a suitable theory to predict the velocities of particles agitated in a turbulent fluid, the velocity of the crystals will have to be estimated.

CRYSTAL-CRYSTAL COLLISIONS

While the velocity of the crystals may be quite high, the difference in velocity between two crystals close enough together to be capable of a collision will be small and a value of 3 cm/s will be assumed. For a 350 μm crystal of ammonium perchlorate, corresponding to about 10 cumulative weight percentage for most of the runs, the energy of collision will be

$$\begin{aligned}&= 0.5 \times 1.952 \times 0.96 \times 0.035^3 \times 3^2 \\ &= 3.6 \times 10^{-4} \text{ ergs.}\end{aligned}$$

The probability of a collision will be proportional to the square of the particle concentration and hence to the square of the number of crystals in suspension. As this has not been found the results are in good agreement with the findings of Clontz and McCabe who suggested that the energy of impact in crystal-crystal collisions would be insufficient to cause appreciable nucleation in continuous crystallizers.

CRYSTAL-VESSEL COLLISIONS

These will be collisions between the crystals and any stationary part of the crystallizer, the walls and the baffles.

Rushton and Oldshue (43) showed theoretically that the velocity of a liquid leaving a turbine impeller was proportional to the speed and

diameter of the impeller. Sachs and Rushton (44) showed this to be so experimentally by photographing the movement of small particles agitated in water, the flow pattern induced by the impeller being shown in fig 5.2. They found that the maximum radial velocity of the particles was in the plane of the impeller and, as the difference in velocity between a crystal and the liquid will be small, the greatest impact of a crystal against the vessel wall will be in this plane. From their results the velocity of liquid leaving the impeller was about a quarter of the tip speed of the impeller and remained virtually constant with radial distance, finally falling to about one sixth of the tip speed of the impeller in the region of the vessel wall. For the 7.41 cm diameter impeller rotating at 600 rpm the tip speed will be 2.3 m/s and a reasonable figure for the impact velocity of the crystal at the vessel wall will be 40 cm/s. The energy of impact for a 350 μ m crystal will then be

$$\begin{aligned}
 &= 0.5 \times 1.952 \times 0.96 \times 0.035^3 \times 40^2 \\
 &= 0.064 \text{ ergs.}
 \end{aligned}$$

The probability of a collision will be proportional to number of crystals arriving at the vessel wall in unit time i.e. proportional to the number of crystals in suspension and the radial velocity of the crystals in the vessel, which will be proportional to the speed and diameter of the impeller.

These dependences have not been found experimentally which together with the low figure for the impact energy suggests that this type of collision is not predominant in the overall nucleation process.

CRYSTAL-IMPELLER COLLISIONS

Taking the closing speed of the impeller with a crystal as the

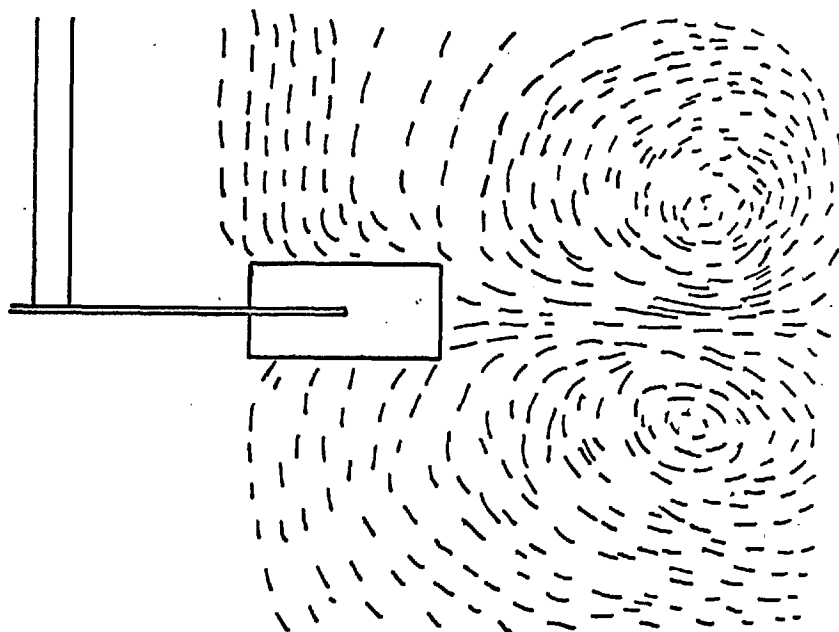


Fig 5.2 Flow pattern induced by a turbine impeller

impact velocity, for the agitation conditions above a reasonable impact velocity would be 2.9 m/s. The impact energy for a 350 μm crystal would then be

$$\begin{aligned} &= 0.5 \times 1.952 \times 0.96 \times 0.035^3 \times 290^2 \\ &= 3.38 \text{ ergs.} \end{aligned}$$

This is quite clearly the most energetic of the three types of collision possible and would be expected to be responsible for the majority of the nucleation, as suggested by Clontz and McCabe (15).

The probability of this type of collision will be discussed in the next section.

5.4 THE EFFECT OF CRYSTAL SURFACE AREA

In section 4.6 it was stated that the correlation between the nucleation rate and the surface area of the suspended crystals was better than that between the nucleation rate and the number of suspended crystals. A similar dependence on the surface area was found by Bransom, Brown and Heeley (8) for magnesium sulphate heptahydrate and by Cise and Randolph (14) for potassium sulphate. This result is rather surprising and could be caused by two alternatives; 1) the number of nuclei produced by a collision is proportional to the surface area of the crystal, 2) the probability of a collision with the impeller is proportional to the cross-sectional area of the crystal.

Two possibilities may be suggested corresponding to the two mechanisms for the formation of secondary nuclei. If the nuclei are formed by crystal breakage then there may be "preferred sites" on the surface of the crystal, for example growth spirals, which will produce nuclei on a collision. If the number of "preferred sites" is proportional to the area of the crystal then the rate of nucleation will be proportional to the surface area of the crystal.

If the nucleation is produced in the laminar layer of the crystal then the number of solute clusters present would be proportional to the surface area of the crystal and would be removed to form nuclei after a suitable collision.

Clontz and McCabe (15) found that the number of nuclei produced after an impact was proportional to the area of contact. If the nucleation is caused by a crystal sliding or scraping along the impeller blade then the area of contact would be proportional to the surface area of the crystals. This is analogous to the crystal sliding experiments of Lal, Mason and Strickland-Constable (20) who found that the number of nuclei produced was independent of the rate of slide of the crystal and therefore presumably dependent on the area of the crystal in contact with the tube.

From the flow pattern of the crystals in the vicinity of the impeller (fig 5.2) the sliding of a crystal along the blade of the impeller as it imparts energy to the liquid is reasonable. The probability of this type of collision will be proportional to the number flux of the crystals, i.e. the concentration and velocity of the crystals, and the rate at which this flux is cut by an impeller blade.

The velocity of the crystals has been shown to be proportional to the speed, N , and diameter, D , of the impeller so for a crystal of size l the probability will be given by:

$$\text{probability} \propto q \, dl \times N \cdot D \times N \quad 5.3$$

where $q \, dl$ is the number of crystals in suspension in the size range l to $l+dl$. If the number of nuclei produced by a slide is proportional to the surface area of the crystal then:

$$\text{nucleation rate} \propto q \, dl \times N \cdot D \times N \times l^2. \quad 5.4$$

Integrating this equation for all crystal sizes:

$$N_0 \propto N^2 D \int_0^\infty q l^2 dl$$

$$\propto N^2 D \times A \quad 5.5$$

where A is the total surface area of the crystals. This relationship is the one found experimentally and suggests that the nucleation is produced by the crystals sliding along the impeller blades.

Whether this mechanism is physically credible is at present a matter of personal judgement, but it is suggested to account numerically for the very definite but simple mathematical relationship found between the observed variables.

5.5 APPLICATION OF THE RESULTS TO LARGE SCALE CRYSTALLIZERS

The rate of growth of ammonium perchlorate has been found proportional to the fourth root of the power input to the crystallizer, which from equation 4.1.2 gives:-

$$\begin{aligned} \frac{dl}{dt} &\propto (N^3 D^5)^{\frac{1}{4}} \\ &\propto N^{\frac{3}{4}} D^{5/4} \end{aligned} \quad 5.6$$

and the rate of nucleation has been found to be given by:

$$N_0/A \propto N^2 D \quad 5.7$$

As the exponents of the impeller speed and diameter, N and D, are not the same in equations 5.6 and 5.7 the selection of the agitator size will play an important part in the operation of a large scale crystallizer. Two examples will be worked to illustrate this.

EXAMPLE 1

Consider a crystallizer capable of operation with two geometrically similar impellers one of which is twice the diameter of the other. If a stirrer speed of N_1 is required for the smaller impeller, a stirrer speed of N_2 will be required for the larger impeller operating at the

same power input given by:

$$\begin{aligned}\frac{N_2}{N_1} &= \left(\frac{D_1}{D_2}\right)^{5/3} \\ &= 0.5^{5/3} \\ &= 0.316\end{aligned}$$

If the area of suspended crystals remains the same when operating with two impellers the ratio of the rates of nucleation will be

$$\begin{aligned}\frac{(N_o)_2}{(N_o)_1} &= \frac{N_2^2 D_2}{N_1^2 D_1} \\ &= 0.316^2 \times 2 \\ &= 0.2\end{aligned}$$

Thus by using an impeller twice the size of a smaller one the nucleation rate is reduced by a factor of five if the impellers are operated at the same power input. If the nucleation rate is reduced then the crystallizer with the larger impeller can either be operated at a larger output than the smaller one to give the same crystal size distribution, or it will produce larger crystals than the smaller one if the output is the same.

While this comparison does not take into account the effect of the other operating variables, comparison of run 19/10 in 7.41 cm, 500 rpm series with run 3/9 in 4.98 cm, 1000 rpm series illustrates the point:

Run	19/10	3/9
Impeller diameter (cm)	7.41	4.98
Power input (W)	5.4	5.5
Supersaturation (%)	0.63	0.61
Production rate (g/s)	0.121	0.062
Crystal size L (μm)	70.2	54.3

With the crystallizer operating at approximately the same power input and supersaturation, use of the larger impeller produced larger crystals at twice the output.

EXAMPLE 2

Consider a scale-up of a pilot scale crystallizer to a larger plant, the scale-up being by a linear factor of 10. In order to maintain the same power input per unit volume the larger impeller will rotate at a speed N_2 given by:

$$\begin{aligned}\frac{N_2}{N_1} &= \left(\frac{D_1}{D_2} \right)^{2/3} \\ &= 0.1^{2/3} \\ &= 0.216\end{aligned}$$

Again if the area of the suspended crystals per unit volume remains the same, the ratio of the rates of nucleation per unit volume will be

$$\begin{aligned}\frac{(N_o)_2}{(N_o)_1} &= \frac{N_2^2 D_2}{N_1^2 D_1} \\ &= 0.216^2 \times 10 \\ &= 0.47\end{aligned}$$

Thus the nucleation rate per unit volume will be approximately half that of the pilot plant and the conclusions drawn at the end of example 1 apply. This decrease in the nucleation rate may not be found in the larger crystallizer as other factors, for example the area and temperature of the cooling surface, may play a more dominant role in which case the majority of the nucleation may not be caused by collisions between the impeller and the suspended crystals.

However these two examples indicate the importance of the selection of the agitator in continuous crystallizers and would favour the selection of as large an impeller as possible if large crystals are required from the crystallizer. They may also explain the popularity of the draft tube type of crystallizer, which uses a large propeller turning at relatively low speed, to obtain low rates of nucleation and consequently large crystals.

5.6 SUMMARY AND CONCLUSIONS

1. A mathematical analysis of the size distribution obtained from a continuous-stirred-tank type of crystallizer has been developed, which allows for a variation of crystal growth rate with crystal size;
2. In a continuous crystallizer the rate of growth of ammonium perchlorate crystals has been found to be linear with supersaturation, independent of the crystal size and proportional to the fourth root of the power input to the crystallizer;
3. The rate of nucleation in the agitated bed of ammonium perchlorate crystals has been found to be proportional to the surface area of the crystals suspended in the crystallizer, the rate of nucleation per unit area of suspended crystal is:
a power law dependence on supersaturation,
proportional to the square of the impeller speed and the impeller diameter.
4. A possible explanation of the above results may be that the majority of the nucleation in an agitated bed of crystals is produced by collisions between the crystals and the impeller. It is not possible to deduce the precise mechanism for the

production of nuclei after a collision and two alternate mechanisms have been discussed involving fracture of the crystal and production of quasi-crystalline clusters of solute molecules in the surface layer surrounding a crystal.

APPENDIX THE COMPUTER PROGRAM

Program Language Algol 60

List of variables:-

ARG	argument for the Gamma function
LGAM	$\ln (\text{Gamma} (\text{arg}))$
PASS	number of passes in the minimization procedure
NOTURNS	number of iterations in the minimization procedure
EXIT	exit conditions from the minimization procedure
CALL	number of function evaluations in the minimization procedure
BIGL	the value of L assuming n is zero
X	crystal size
Y	experimental cumulative weight fraction
Z	calculated cumulative weight fraction
MEANL	mean value of BIGL
P	the parameters L and n to be minimized
S 0,1,2	the sum of the squares of the errors at points 0,1,2
Q 0,1	estimated reduction in S at points 1,2
T	step length multiplier
L	step length
Q,W,A	constants in cubical interpolation
B	approximation to the inverse matrix of the second derivatives. It is set to the unity matrix at the start of the process and is updated at each iteration
AA,BB	modifiers to the matrix B
P 0,1,2	values of the parameters to be minimized at points 0,1,2
DP 0,1,2	values of $\partial S / \partial P$ at points 0,1,2
DELP 1,2	ΔP to get to points 1,2

```

MIP720 MINIMISATION GAMMA4 AND CURVE FIT;
"BEGIN" "REAL" P2,ARG,LGAM;
  "INTEGER" "ARRAY" TITLE[1:120],N[1:2];
  "INTEGER" I,J,PASS,NOTURNS,EXIT,CALL;
  "ARRAY" BIGL,X,Y[1:2,1:30],Z[1:30],MEANL,P[1:2];
  "BOOLEAN" CHECK,FIRSTTIME; "SWITCH" SW:=NEXT,REPEAT;

"CODE" "REAL" "PROCEDURE" LGAMMA(Z); "VALUE" Z; "REAL" Z;
  "ALGOL";
"CODE" "REAL" "PROCEDURE" GAMMAA(A,X,LGAM);
  "VALUE" A,X,LGAM; "REAL" A,X,LGAM;
  "ALGOL";
"CODE" "BOOLEAN" "PROCEDURE" IFL2;
  "ALGOL";
"CODE" "BOOLEAN" "PROCEDURE" IFL3;
  "ALGOL";

"PROCEDURE" PRINT5(X); "VALUE" X; "REAL" X;
"BEGIN" "REAL" XX; "INTEGER" I;
XX:=ABS(X);
I:="IF" XX<1.31*5 "THEN" X "ELSE" 0;
"IF" XX<=-18 "THEN" "PRINT" "S6"0"S5"
  "ELSE" "IF" ABS(X-I)<=-18 "THEN" "PRINT" SAMELINE,
    DIGITS(6),"S2",I,"S3"
  "ELSE" "IF" XX "GE" 5 "OR" XX<=-3 "THEN" "PRINT" SAMELINE,
    SCALED(5),X,"S"
  "ELSE" "IF" XX<5 "AND" XX "GE" -1 "THEN" "PRINT" SAMELINE,
    FREEPOINT(5),"S2",X,"S3"
  "ELSE" "IF" XX<=-1 "AND" XX "GE" -2 "THEN" "PRINT" SAMELINE,
    FREEPOINT(6),"S2",X,"S2"
  "ELSE" "PRINT" SAMELINE,FREEPOINT(7),"S2",X,"S"
"END" OF PRINT5;

"PROCEDURE" COPY(P1,P2); "VALUE" P2; "ARRAY" P1,P2;
"BEGIN" P1[1]:=P2[1]; P1[2]:=P2[2];
"END" OF COPY;

"COMMENT" HALTCODE. THE PLOTTER INSTRUCTIONS ARE INSERTED
HERE. THESE ARE A SET OF INSTRUCTIONS IN ALGOL AND CONTAIN
THE FOLLOWING PROCEDURES:-
  AXES, FOR DRAWING THE AXES OF THE GRAPH
  MOVESPEN(X,Y,I), FOR MOVING THE PEN TO X,Y
  DRAWSLINE(X,Y,I), FOR DRAWING A LINE FROM THE CURRENT
    POSITION TO X,Y
  CHAR(I), FOR DRAWING SYMBOLS I
  WAY, FOR ALTERING THE SIZE OF PRINTED CHARACTERS;

```

```

"REAL" "PROCEDURE" INVERTGAMMA(X,Z);
  "VALUE" X,Z; "REAL" X,Z;
  INVERTGAMMA:=(((X/6+0.5)*X+1)*X+1-(Z)*EXP(X));

"REAL" "PROCEDURE" SOLVEX(Z); "VALUE" Z; "REAL" Z;
"BEGIN" "BOOLEAN" BD; "REAL" X,X1,X2;
X:=X1:=0.1; X2:=15; BD:=INVERTGAMMA(X,Z)>0;
"FOR" X:=(X1+X2)/2 "WHILE" ABS(X1-X2)>.5 "DO"
  "BEGIN" "IF" INVERTGAMMA(X,Z)>0 "THEN"
    "BEGIN" "IF" BD "THEN" X1:=X "ELSE" X2:=X "END"
    "ELSE" "IF" BD "THEN" X2:=X "ELSE" X1:=X "END";
  SOLVEX:=X;
"END" OF SOLVEX;

"PROCEDURE" USEMODEL(P,Z); "VALUE" P; "ARRAY" P,Z;
"BEGIN" "INTEGER" I;
CALL:=CALL+1;
P2:=P[2]; ARG:=(4-P2)/(1-P2); LGAM:=LGAMMA(ARG);
"FOR" I:=1 "STEP" 1 "UNTIL" N[1] "DO"
  Z[I]:=GAMMA(ARG,(X[1,I]/(100*P[1]))+(1-P2),LGAM);
"END" OF USEMODEL;

"BOOLEAN" "PROCEDURE" CONSTRAINTS(P);
  "VALUE" P; "ARRAY" P;
  CONSTRAINTS:=P[1]<= -3 "OR" P[2]>0.9;

"REAL" "PROCEDURE" CRIT(P); "VALUE" P; "ARRAY" P;
"BEGIN" "REAL" S; "INTEGER" I;
USEMODEL(P,Z); S:=0;
"FOR" I:=1 "STEP" 1 "UNTIL" N[1] "DO"
  S:=S+(Z[I]-Y[1,I])*2;
CRIT:=S;
"END" OF CRIT;

"PROCEDURE" DIFF(S,P,DP);
  "VALUE" S,P; "REAL" S; "ARRAY" P,DP;
"BEGIN" "REAL" DELS; "INTEGER" I; "ARRAY" DELP[1:2];
COPY(DELP,P);
"FOR" I:=1,2 "DO"
  "BEGIN" DELP[I]:=P[I]+.5;
  DELS:=CRIT(DELP);
  DP[I]:=(DELS-S)*.5;
  DELP[I]:=P[I];
  "END"
"END" OF DIFF;

```

```

"PROCEDURE" DOUBLEFIT(P0); "ARRAY" P0;
"BEGIN" "REAL" S0,S1,S2,Q,Q0,Q1,T,L,W,A,C,D,SUM1,SUM2,RATIO;
      "INTEGER" J,I,K; "ARRAY" B,AA,BB[1:2,1:2];
      "ARRAY" P1,P2,DP0,DP1,DP2,DELP1,DELP2,S,R,CC[1:2];
      "SWITCH" SW:=L0,L1,L30,L7,L31,L01,L11,L12;

"PROCEDURE" CAPTION(NO); "VALUE" NO; "INTEGER" NO;
"BEGIN" "INTEGER" I; "REAL" SUM1,SS,R;
"IF" NO=1 "THEN" "PRINT" 'L2 STARTING VALUES LS5';
      "ELSE" "PRINT" 'L2 FINAL VALUES LS5';
"PRINT" 'P1 S10 P2 L'; PRINT5(P0[1]); PRINT5(P0[2]);
SS:=S0;
"PRINT" 'L SUM OF ERRORS SQUARED'; PRINT5(SS);
R:=SQRT(SS/(N[1]-2));
SUM1:=0;
"FOR" I:=1 "STEP" 1 "UNTIL" N[1] "DO"
      SUM1:=SUM1+ABS(Z[I]-Y[1,I]);
SUM1:=SUM1/N[1];
"PRINT" 'L RESIDUALS STANDARD DEVIATION'; PRINT5(R);
"PRINT" 'L RESIDUALS VARIATION'; PRINT5(SS/SUM1);
"END" OF CAPTION;

NOTURNS:=PASS:=0;
S0:=CRIT(P0);
CAPTION(1);
B[1,1]:=B[2,2]:=1; B[1,2]:=B[2,1]:=0;

DIFF(S0,P0,DP0);
L0: CHECK:=IFL2 "OR" "NOT"(CHECK "IMPL" IFL3);
T:=1; Q0:=0;
"FOR" J:=1,2 "DO"
      "BEGIN" S[J]:=0;
      "FOR" K:=1,2 "DO" S[J]:=S[J]-B[J,K]*DP0[K];
      Q0:=Q0+S[J]*DP0[J];
      "END";

"IF" ABS(Q0/S0)<= -5 "AND" NOTURNS>2 "THEN"
      "BEGIN" EXIT:=3; "GOTO" L11 "END";

L:=-2*S0/Q0;
"IF" ABS(L)>1 "THEN" L:=L/ABS(L);

L1: L:=T*L;
CHECK:=IFL2 "OR" "NOT"(CHECK "IMPL" IFL3);
"IF" CHECK "THEN" "PRINT" PUNCH(3), 'L P1';
"FOR" J:=1,2 "DO"
      "BEGIN" DELP1[J]:=L*S[J];
      P1[J]:=P0[J]+DELP1[J];
      "IF" CHECK "THEN" "PRINT" PUNCH(3),P1[J];
      "END";
"IF" CONSTRAINTS(P1) "THEN" "GOTO" L30;
S1:=CRIT(P1);
"IF" CHECK "THEN" "PRINT" PUNCH(3),ALIGNED(3,7), 'L',S1;
"IF" S1<0 "THEN" "GOTO" L30 "ELSE" "GOTO" L7;

```

```

L30: "IF" T<5. -9 "THEN"
      "BEGIN" "PRINT" "L NO FURTHER PROGRESS MADE";
      "GOTO" L11
      "END";
T:=0.95*T+2;
PASS:=PASS+1;
"GOTO" L1;

L7: DIFF(S1,P1,DP1);
Q1:=0;
"FOR" J:=1,2 "DO" Q1:=Q1+S[J]*DP1[J];

"IF" L*Q1<0 "AND" S1<S0
      "THEN" "BEGIN" "IF" T=1 "AND" ABS(Q1)<ABS(Q0)
        "THEN" "BEGIN" L:=2*L; "GOTO" L1 "END"
        "ELSE" "BEGIN" S0:=S1; Q0:=Q1;
          COPY(P0,P1); COPY(DP0,DP1);
          "GOTO" L0
        "END"
      "END";

Q:=3*(S0-S1)/L+Q0+Q1;
W:=SQRT(Q+2 - Q0*Q1);
A:=L*(Q+W-Q0)/(Q1+2*W-Q0);
"IF" CHECK "THEN" "PRINT" PUNCH(3), "L P2";
"FOR" J:=1,2 "DO"
      "BEGIN" DELP2[J]:=A*S[J];
      P2[J]:=P0[J]+DELP2[J];
      "IF" CHECK "THEN" "PRINT" PUNCH(3),P2[J];
      "END";
"IF" CONSTRAINTS(P2) "THEN" "GOTO" L30;
S2:=CRIT(P2);
"IF" CHECK "THEN" "PRINT" PUNCH(3),ALIGNED(3,7), "L",S2;
"IF" S2 "LE" S0 "AND" S2 "LE" S1
      "THEN" "GOTO" L31 "ELSE" "GOTO" L30;

L31: "IF" ABS(S2-S1)< -5*S2 "AND" ABS(S2-S0)< -5*S2
      "AND" NOTURNS>3 "THEN"
        "BEGIN" EXIT:=2; COPY(P0,P2); "GOTO" L11
        "END";

DIFF(S2,P2,DP2);
C:=D:=0;
"FOR" J:=1,2 "DO"
      "BEGIN" R[J]:=DP2[J]-DP0[J];
      C:=C+DELP2[J]*R[J];
      "END";
"FOR" J:=1,2 "DO" "FOR" K:=1,2 "DO"
      "BEGIN" D:=D+B[J,K]*R[J]*R[K];
      AA[J,K]:=DELP2[J]*DELP2[K]/C;
      "END";
"FOR" K:=1,2 "DO"
      "BEGIN" CC[K]:=0;
      "FOR" J:=1,2 "DO" CC[K]:=CC[K]+B[J,K]*R[J];
      "END";
"FOR" J:=1,2 "DO" "FOR" K:=1,2 "DO"
      "BEGIN" BB[J,K]:=-CC[J]*CC[K]/D;
      B[J,K]:=B[J,K]+AA[J,K]+BB[J,K];
      "END";

```

```

S0:=S2; COPY(P0,P2); COPY(DP0,DP2);
NOTURNS:=NOTURNS+1;
"IF" CHECK "THEN" "PRINT"PUNCH(3), 'L' END OF ITERATION, NOTURNS;
"IF" NOTURNS "LE" 2 "THEN" "GOTO" L0;

"FOR" J:=1,2 "DO"
  "BEGIN" RATIO:=ABS(DELP2[J]/P0[J]);
  "IF" RATIO "GE" 2e-4 "OR" RATIO "GE" 5e-4*ABS(A)
    "THEN" "GOTO" L0;
  "END";
L01: SUM1:=SUM2:=0;
"FOR" J:=1,2 "DO"
  "BEGIN" SUM1:=SUM1+S[J]^2;
  SUM2:=SUM2+P0[J]^2;
  "END";
RATIO:=ABS(A)*SQRT(SUM1/SUM2);
"IF" RATIO<= -3*ABS(A) "AND" RATIO<= -3
  "THEN" "BEGIN" EXIT:=4; "GOTO" L11 "END"
  "ELSE" "GOTO" L0;

L11: CAPTION(2);
L12: "END" OF DOUBLEFIT;

"COMMENT" START OF PROGRAM;
SAMELINE;
CHECK:=IFL2 "AND" IFL3;
CHECK:=FIRSTTIME:="FALSE";
REPEAT: FIRSTTIME:="NOT" FIRSTTIME;
ADVANCE(1); "IF" BUFFER(1, '/') "THEN" STOP;
"IF" FIRSTTIME "THEN" "BEGIN" I:=J:=1; INSTRING(TITLE,J);
  J:=1; PUNCH(1); "PRINT" 'L10', OUTSTRING(TITLE,J), 'L2';
  AXES(2,50,0.05,0,200,0.2,6,0,5,0,0,0);
  MOVESPEN(100,-0.1,0); WAY(0,8); PUNCH(5);
  J:=1; OUTSTRING(TITLE,J); J:=80 "END"
"ELSE" "BEGIN" I:=2; J:=100 "END";
INSTRING(TITLE,J);

N[I]:=0;
NEXT: N[I]:=N[I]+1; "READ" X[I,N[I]],Y[I,N[I]];
ADVANCE(1); "IF" "NOT" BUFFER(1, '*') "THEN" "GOTO" NEXT;

MEANL[I]:=0;
"FOR" J:=1 "STEP" 1 "UNTIL" N[I] "DO"
  "BEGIN" BIGL[I,J]:=X[I,J]/SOLVEX(Y[I,J]);
  MEANL[I]:=MEANL[I]+BIGL[I,J];
  "END";
MEANL[I]:=MEANL[I]/N[I]; LGAM:=LGAMMA(4);

```

```

J:="IF" FIRSTTIME "THEN" 80 "ELSE" 100;
PUNCH(1); OUTSTRING(TITLE,J);
"PRINT" "L2 MEAN VALUE OF L =",FREEPOINT(S),MEANL[I],
  ' MICRONS L2S5 L S8 Z S5 GAMMA Z S5 BIGL';
"FOR" J:=1 "STEP" 1 "UNTIL" N[I] "DO"
  "PRINT" "L",FREEPOINT(S),ENTIER(X[I,J]),PREFIX('S3'),
    Y[I,J],GAMMAA(4,X[I,J]/MEANL[I],LGAM),BIGL[I,J];
"PRINT" "L2";

"IF" FIRSTTIME "THEN" "GOTO" REPEAT "ELSE" "PRINT" "R60";

"FOR" I:=1,2 "DO"
  "BEGIN" "FOR" J:=1 "STEP" 1 "UNTIL" N[I] "DO"
    MOVESPEN(X[I,J],Y[I,J],I);
    MOVESPEN(0,1,0); DRAWSLINE(10,1,0);
    "FOR" J:=20 "STEP" 10 "UNTIL" X[I,1]+30 "DO"
      DRAWSLINE(J,GAMMAA(4,J/MEANL[I],LGAM),0);
    "IF" MEANL[1]>MEANL[2]
      "THEN" "BEGIN" "IF" I=1
        "THEN" "BEGIN" MOVESPEN(MEANL[1]*3.7+200,0.7,I);
          J:=80 "END"
        "ELSE" "BEGIN" MOVESPEN(MEANL[1]*3.7+150,0.65,I);
          J:=100 "END"
      "END"
      "ELSE" "IF" I=1
        "THEN" "BEGIN" MOVESPEN(MEANL[2]*3.7+150,0.65,I);
          J:=80 "END"
        "ELSE" "BEGIN" MOVESPEN(MEANL[2]*3.7+200,0.7,I);
          J:=100 "END";
    WAY(0,6); PUNCH(5); "PRINT" "S"; OUTSTRING(TITLE,J);
  "END" OF PLOTTING;

PUNCH(1); CHECK:=IFL2 "OR" "NOT"(CHECK "IMPL" IFL3);

"IF" ABS(MEANL[1]-MEANL[2])>MEANL[1]/10
  "THEN" "BEGIN" "IF" "NOT" CHECK
    "THEN" "BEGIN" MOVESPEN(0,1.4,0); "GOTO" REPEAT "END"
  "END";

J:=1; "PRINT" "L10",OUTSTRING(TITLE,J);
CALL:=0;
P[1]:=MEANL[1]/100; P[2]:=0;
DOUBLEFIT(P);
"PRINT" "L LEAST SQUARES FIT L EXIT CONDITION, EXIT,
  ' L NUMBER OF PASSES, PASS,
  ' L NUMBER OF ITERATIONS, NOTURNS,
  ' L NUMBER OF FUNCTION EVALUATIONS, CALL, LR60";

P2:=P[2]; ARG:=(4-P2)/(1-P2); LGAM:=LGAMMA(ARG);
MOVESPEN(0,1,0); DRAWSLINE(10,1,0);
"FOR" J:=20 "STEP" 10 "UNTIL" X[1,1]+30 "DO"
  "BEGIN" DRAWSLINE(J,GAMMAA(ARG,(J/(P[1]*100))+(1-P2),LGAM),0);
  "IF"(J "DIV" 80)*80 = J "THEN" "BEGIN" CHAR(3); CHAR(4) "END"
  "END";
MOVESPEN(0,1.4,0); "GOTO" REPEAT;
"END"
"END" OF PROGRAM;

```

NOTES ON THE SIR PROCEDURE GAMMAA

function code	operation
0	load B register
1	add contents of address to accumulator
2	negate accumulator and add contents of address
4	load contents of address into accumulator
5	store accumulator into address
7	jump to address if accumulator is zero
8	jump to address
9	jump to address if accumulator is negative
10	add 1 to contents of address
11	store sequence control register
14	shift accumulator n places to the left

Function routines used in the interpreter

31	$R1 + R2$
33	$R1 - R2$
35	$R1 \times R2$
37	$R1 / R2$
60	$\exp(R1)$
61	$\ln(R1)$

[GAMMAA]

GAMMAA /14 3

+0

0 38

/4 6

7 XZERO

5 X

5 BNM2

5 R6

/4 7

5 X+1

5 BNM2+1

5 R6+1

/4 8

5 X+2

5 BNM2+2

5 R6+2

1 +5

9 XZERO

/4 3

5 A

5 R8

/4 4

5 A+1

5 R8+1

/4 5

5 A+2

5 R8+2

4 ONE

5 ANM2

5 ANM1

5 R7

4 ONE+1

5 ANM2+1

5 ANM1+1

5 R7+1

4 ONE+2

5 ANM2+2

5 ANM1+2

5 R7+2

SET

0 50

4 INSTR1

/5 34

4 INSTR1+1

/5 36

4 PR7

5 80

0 40

/0 33

/11 0

/8 1

```

      4 PR6
      5 80
      0 40
    /0 31
    /11 0
    /8 1          (BNM1 IN R6)
      4 R6
      5 BNM1
      4 R6+1
      5 BNM1+1
      4 R6+2
      5 BNM1+2
      4 +2
      5 N
      4 +1
      5 ODD
REPEAT 4 ODD
      2 +0
      5 ODD          (-1=TRUE)
      4 ANM1
      5 R1
      4 ANM1+1
      5 R1+1
      4 ANM1+2
      5 R1+2          (ANM1 IN R1)
      4 BNM1
      5 R6
      4 BNM1+1
      5 R6+1
      4 BNM1+2
      5 R6+2          (BNM1 IN R6)
      4 ODD
      9 TRUE1
      4 ONE
      5 R7
      4 ONE+1
      5 R7+1
      4 ONE+2
      5 R7+2
      8 FALSE
TRUE1 4 X
      5 R7
      4 X+1
      5 R7+1
      4 X+2
      5 R7+2
FALSE 4 R7
      5 R2
      4 R7+1
      5 R2+1
      4 R7+2
      5 R2+2          (BBN IN R2 AND R7)
      4 PR1
      5 80
      0 40
    /0 35
    /11 0
    /8 1          (ANM1*BBN IN R1)

```

```

4 PR6
5 80
0 40
/0 35
/11 0
/8 1          (BNM1*BBN IN R6)
10 N
4 N
14 8191
5 83
4 +0
5 84
4 +17
5 85
0 50
/11 0
/8 1          (N DIV 2 IN REAL)
4 83
5 R2
4 84
5 R2+1
4 85
5 R2+2        (N DIV 2 IN R2)
4 ODD
9 TRUE2       (JUMP IF TRUE)
4 A
5 R3
4 A+1
5 R3+1
4 A+2
5 R3+2        (A IN R3)
4 PR2
5 80
0 40
/0 33
/11 0
/8 1          (AAN IN R2)
TRUE2 4 R2
5 R7
4 R2+1
5 R7+1
4 R2+2
5 R7+2        (AAN IN R7)
4 ANM2
5 R3
4 ANM2+1
5 R3+1
4 ANM2+2
5 R3+2        (ANM2 IN R3)
4 BNM2
5 R8
4 BNM2+1
5 R8+1
4 BNM2+2
5 R8+2        (BNM2 IN R8)

```

```

      4 PR2
      5 80
      0 40
    /0 35
    /11 0
    /8 1      (ANM2*AAN IN R2)
      4 PR7
      5 80
      0 40
    /0 35
    /11 0
    /8 1      (BNM2*AAN IN R7)
      4 PR1
      5 80
      0 40
    /0 31
    /11 0
    /8 1      (AN IN R1)
      4 PR6
      5 80
      0 40
    /0 31
    /11 0
    /8 1      (BN IN R6)
UPDATE  4 ANM1
        5 ANM2
        4 ANM1+1
        5 ANM2+1
        4 ANM1+2
        5 ANM2+2
        4 BNM1
        5 BNM2
        4 BNM1+1
        5 BNM2+1
        4 BNM1+2
        5 BNM2+2
        4 R1
        5 ANM1
        4 R1+1
        5 ANM1+1
        4 R1+2
        5 ANM1+2
        4 R6
        5 BNM1
        4 R6+1
        5 BNM1+1
        4 R6+2
        5 BNM1+2
CHECK1  4 BNM1
        7 REPEAT (GOTO REPEAT IF BNM1=0)
        4 BNM2
        7 REPEAT (GOTO REPEAT IF BNM2=0)
        4 ANM1
        5 R1
        4 ANM1+1
        5 R1+1
        4 ANM1+2
        5 R1+2      (ANM1 IN R1)

```

```

4 BNM1
5 R2
4 BNM1+1
5 R2+1
4 BNM1+2
5 R2+2      (BNM1 IN R2)
4 PR1
5 80
0 40
/0 37
/11 0
/8 1      (ANM1/BNM1 IN R1)
4 ANM2
5 R7
4 ANM2+1
5 R7+1
4 ANM2+2
5 R7+2      (ANM2 IN R7)
4 BNM2
5 R8
4 BNM2+1
5 R8+1
4 BNM2+2
5 R8+2      (BNM2 IN R8)
4 PR7
5 80
0 40
/0 37
/11 0
/8 1      (ANM2/BNM2 IN R7)
4 R1
5 R6
4 R1+1
5 R6+1
4 R1+2
5 R6+2      (ANM1/BNM1 IN R6)
4 PR6
5 80
0 40
/0 33
/11 0
/8 1      (DIFF IN R6)
CHECK2 4 R6
7 OUT      (GOTO OUT IF DIFF=0)
4 R6+2
1 +20
9 OUT      (GOTO OUT IF DIFF<0-6)
8 REPEAT
OUT 4 A
5 R2
4 A+1
5 R2+1
4 A+2
5 R2+2      (A IN R2)

```

```

4 X
5 R3
4 X+1
5 R3+1
4 X+2
5 R3+2      (X IN R3)
4 PR3
5 80
0 40
/0 61
/11 0
/8 1      (LN X IN R3)
4 PR2
5 80
0 40
/0 35
/11 0
/8 1      (A*LN X IN R2)
4 X
5 R3
4 X+1
5 R3+1
4 X+2
5 R3+2      (X IN R3)
0 38
/4 9
5 R4
/4 10
5 R4+1
/4 11
5 R4+2      (LGAM IN R4)
4 PR3
5 80
0 40
/0 31
/11 0
/8 1      (X+LGAM IN R3)
4 PR2
5 80
0 40
/0 33
/11 0
/8 1      (A*LN X - X - LGAM IN R2)
4 PR2
5 80
0 40
/0 60
/11 0
/8 1      (EXP IN R2)
RESET 0 50
4 INSTR2
/5 34
4 INSTR2+1
/5 36

```

```

      4 PR1
      5 80
      0 40
    /0 35
  /11 0
    /8 1      (ANSWER IN R1)
      4 R1+2
      2 +0
      9 XZERO
      0 38
      4 R1
      9 XZERO
    /5 0
      4 R1+1
    /5 1
      4 R1+2
    /5 2
      8 END
XZERO  0 38
      4 ONE
    /5 0
      4 ONE+1
    /5 1
      4 ONE+2
    /5 2
END     0 GAMMAA+1
      /8 1

ONE     8 0
      0 0
      0 1

R1      >+3
R2      >+3
R3      >+3
R4      >+3
R5      >+3
R6      >+3
R7      >+3
R8      >+3
A       >+3
X       >+3
ANM1    >+3
ANM2    >+3
BNM1    >+3
BNM2    >+3
ODD     +0
N       +0
PR1     0 R1
PR2     0 R2
PR3     0 R3
PR4     0 R4
PR5     0 R5
PR6     0 R6
PR7     0 R7
INSTR1  1 &100000
        1 &600000
INSTR2  1 3653
        1 3654
%
```

BIBLIOGRAPHY

- 1 Abegg, C.F., Stevens, J.D. and Larson, M.A.
A. I. Ch. E. Jl. (1968), 14, 118
- 2 Abromowitz, M. and Stegun, I.A.
Editors - Handbook of Mathematical Functions (1964), 263
(U.S. Dept. of Commerce)
- 3 Ayerst, R.P. and Phillips, M.I.
J. Chem. Engng Data (1966), 11, 494
- 4 Ayerst, R.P. and Phillips, M.I.
"Industrial Crystallization: proc. of Symposium" (1969), 56
(London: Instn of chem. Engrs)
- 5 Ayerst, R.P. and Phillips, M.I.
"Industrial Crystallization: proc. of Symposium" (1969), 177
(London: Instn of chem. Engrs)
- 6 Bennett, R.C.
Chem. Engng Prog. (1962), 58(6), 76
- 7 Bransom, S.H.
Br. chem. Engng (1960), 5, 838
- 8 Bransom, S.H., Brown, D.E. and Heeley, G.P.
"Industrial Crystallization: proc. of Symposium" (1969), 43
(London: Instn of chem. Engrs)
- 9 Bransom, S.H., Brown, D.E. and Watts, P.
"Industrial Crystallization: proc. of Symposium" (1969), 109
(London: Instn of chem. Engrs)
- 10 Bransom, S.H., Dunning, W.J. and Millard, B.
Disc. Faraday Soc. No 5, (1949), 83
- 11 Bujac, P.D.B. and Mullin, J.W.
"Industrial Crystallization: proc. of Symposium" (1969), 121
(London: Instn of chem. Engrs)
- 12 Canning, T.F. and Randolph, A.D.
A. I. Ch. E. Jl. (1967), 13, 5
- 13 Cayey, N.W. and Estrin, J.
Ind. Engng Chem. (Fundamentals) (1967), 6, 13
- 14 Cise, M.D. and Randolph, A.D.
A. I. Ch. E. Symposium Series No 121, (1972), 68, 42
- 15 Clontz, N.A. and McCabe, W.L.
Chem. Engng Prog. Symposium Series No 110, (1971), 67, 6

- 16 Coggan, G.C.
Instn of chem. Engrs Symposium Series No 23, (1967), 32
- 17 Fletcher, R. and Powell, M.J.D.
Computer J. (1963), 6, 163
- 18 Hixson, S.W. and Knox, K.L.
Ind. Engng Chem. (1951), 43, 2144
- 19 Isaac, F.
J. chem. Soc. (1908), 93, 384
- 20 Lal, D.P., Mason, R.E.A. and Strickland-Constable, R.F.
J. Crystal Growth (1969), 5, 1
- 21 McCabe, W.L.
Ind. Engng Chem. (1929), 21, 30; idem ibid, 112
- 22 Mason, R.E.A. and Strickland-Constable, R.F.
Trans. Faraday Soc. (1966), 62, 455
- 23 Matz, G.
Chemie-Ingr-Tech. (1966), 38, 341
- 24 Matz, G.
"Industrial Crystallization: proc. of Symposium" (1969),
discussion p.237. (London: Instn of chem. Engrs)
- 25 Melia, T.P.
J. appl. Chem. (1965), 15, 345
- 26 Melia, T.P. and Moffitt, W.P.
Ind. Engng Chem. (Fundamentals) (1964), 3, 313
- 27 Miers, H.A. and Isaac, F.
J. chem. Soc. (1906), 89, 413
- 28 Mullin, J.W.
"Crystallization" (1961). (London: Butterworths)
- 29 Mullin, J.W., Chakraborty, M. and Mehta, K.
J. appl. Chem. (1970), 20, 367
- 30 Mullin, J.W. and Garside, J.
Trans. Instn chem. Engrs (1967), 45, T291
Idem (1968), 46, T11
- 31 Mullin, J.W., Garside, J. and Gaska, C.
Chem Ind. (1966), 1704
- 32 Mullin, J.W. and Leci, C.L.
Phil. Mag. (1969), 19, 1075
- 33 Nyvlt, J.
J. Crystal Growth (1968), 4, 377

- 34 Nyvlt, J. and Mullin, J.W.
Chem. Engng Science (1970), 25, 131
- 35 Ostwald, W.
"Lehrbuch Vol. II 1896-1906". (Leipzig: Englemann)
- 36 Pearson, K.
"Tables of the Incomplete Gamma Function" (1923) (London: HMSO)
- 37 Powers, H.E.C.
Nature (1956), 178, 139
- 38 Randolph, A.D.
A. I. Ch. E. Jl. (1965), 11, 424
- 39 Randolph, A.D. and Larson, M.A.
A. I. Ch. E. Jl. (1962), 8, 639
- 40 Randolph, A.D. and Rajagopal, K.
Ind. Engng Chem. (Fundamentals) (1970), 2, 165
- 41 Robinson, J.N. and Roberts, J.E.
Can. J. chem. Engng (1957), 35, 105
- 42 Rushton, J.H., Costich, E.W. and Everett, H.J.
Chem. Engng Prog. (1950), 46, 395; Idem ibid, 467
- 43 Rushton, J.H. and Oldshue, J.Y.
Chem. Engng Prog. (1953), 49, 161; Idem ibid, 267
- 44 Sachs, J.P. and Rushton, J.H.
Chem. Engng Prog. (1954), 50, 597
- 45 Saeman, W.C.
A. I. Ch. E. Jl. (1956), 2, 107
- 46 Strickland-Constable, R.F.
"Kinetics and Mechanism of Crystallization" (1968)
(London: Academic Press)
- 47 Strickland-Constable, R.F. and Mason, R.E.A.
Nature (1963), 197, 897
- 48 Ting, H.H. and McCabe, W.L.
Ind. Engng Chem. (1934), 26, 1201
- 49 Volmer, M.
"Kinetic der Phasenbildung" (1939) (Dresden: Steinkopf)