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Signed *H. E. Juck*.....

THE KINETICS OF
SUCROSE CRYSTALLIZATION

by

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INTRODUCTION

This study has been undertaken for two main purposes:-

(1) To obtain factual information concerning the rate of growth of sucrose crystals; and

(2) To secure some understanding of the operating mechanism of factors influencing crystal growth.

Chapter 3 records details of the experimental method used and data gathered for actual growth rates. Associated with these in chapter 2 is set down information believed to have a significant bearing on the mechanism study.

For the mechanism study growth has been looked upon as a physical rate process bearing certain analogies to chemical reactions and mathematical treatment has been carried out with this in mind, it being effectively a kinetic study in an essentially physical system.

Chemical kinetics has to do with the study of rates of chemical reactions and of the influence of conditions upon these rates. The most important experimental conditions are concentrations (or pressures) of reacting substances, temperature, presence of a catalyst and radiation.

In the case of sucrose crystallization the chemical reaction theory is transferred to the physical rate process. The kinetics of sucrose crystallization thus concerns the rate of crystallization of sucrose and the influence of conditions such as concentrations, temperature and impurities.

Crystallization is a process in which the solute molecules move from the solution to the surface of the growing crystal and incorporate themselves into the crystal lattice. The relative influence of the crystal surface and mother liquor may then be examined in the light of rate process kinetics.

The Arrhenius equation, which is the basis of kinetic studies, for chemical reactions may be stated,

$$k = A e^{-E/RT}$$

where k is the velocity constant in the chemical reaction.

In the current studies k is used in this equation as the velocity of crystallization of sucrose and is essentially the physical rate constant of concern in this system. A plot of log k v. 1/T is linear and the activation energy of crystallization (E) may be calculated from the slope of the line.

The constant A in the Arrhenius relationship is essentially a frequency factor in chemically reacting systems and its study has been suitably incorporated in the activated complex theory of reaction rates. While some possible analogies are recognised, the full implications are not insisted upon in the present studies.

The crystallization of sucrose consists of two consecutive stages, firstly, nuclei formation; and secondly, crystal growth. These current studies are essentially concerned with the latter growth process only.

When studying chemically reacting systems, the chemical potential or driving force is the difference between the concentration of reacting material on the one hand and the concentration of the product on the other. In the system of crystallizing sucrose, the driving force is the difference between the concentration of the oversaturated solution and that of a saturated solution.

In this thesis supersaturation (S) is defined as the ratio of the concentration of solution used in experiment expressed in g sucrose / g water to the concentration of a saturated solution at the same temperature and in similar units.

In these current studies some experiments concerning rates of solution have also been carried out, and the rate of solution has been regarded as a negative rate of crystallization.

Viscosity has a vital bearing on the study of the aqueous sucrose crystallizing system, and although the viscosity characteristics of this system are well documented for non-saturated conditions, there does not appear to be very much material concerning saturated and oversaturated concentrations. *

Information in this region and which is relevant to the present studies has been sought experimentally, and is recorded and discussed in chapter 2. A study has also been made of the viscosity characteristics of the sucrose - ethanol - water system with the object of observing changes in viscosity activation energies and discussing their bearing on crystallization mechanisms. These are likewise recorded in chapter 2.

*Last ICUMSA reports (Copenhagen) contain viscosity data up to 86% solutions and 80°.

CHAPTER 1. REVIEW OF LITERATURE.1. MEASURING RATES OF CRYSTAL GROWTH.

Various techniques have been recorded in the literature from time to time for the purpose of measuring the actual rates of crystal growth. These involve essentially measurement of the crystal or measurement of solution concentration.

(A) MEASUREMENT OF THE CRYSTAL.

It is direct microscopic and projection measurements of the size of growing crystals or of their weights. Kucharenko¹ gained his elaborate data by this method. He chose large (2-12 g.) well-formed crystals and grew them in supersaturated syrups. He estimated the growing surface from the formula,

$$\sigma^3 = Cp^2 \quad (1-1)$$

By tedious measurements he found that the value of C ranged from 63.2 to 76.0 for 13 crystals, an average of 69.93.

Smythe² has developed a method for measuring the rate of crystallization of sucrose from pure and impure solutions with a satisfactory degree of accuracy. It has the advantage of using single crystals. Such factors as crystal surface area, the relative velocity of crystal and solution, and concentration of the solution, can be ascertained or directed with greater precision than is the case with other methods. He found that with pure solutions the rate of crystallization can be accurately determined by weighing the crystal before and after immersion in a sucrose solution for a definite time (1-3 hours). The crystals used were between 40 and 150 mg, and the rate of crystallization was calculated in the same way as by Kucharenko.

(B) MEASUREMENT OF SOLUTION CONCENTRATION.

This is a relative method which utilises the change in concentration of a supersaturated solution in which the crystal seeds are suspended. The best properties for the determination

are refractive index and density.

Whittier and Gould³ followed the course of crystallization by successive refractometer readings on sucrose solutions at 30°, 25°, 20°, 15°, 10° and 0°. Crystallizations were effected in a flask which was immersed in a thermostat. Initial concentration of each solution was ascertained by a refractometer reading on a few drops of solution. 5 g of fine seed sucrose crystals were then added for each 100 g of solution, and stirring was started simultaneously. The rate of stirring during crystallization was always above 400 r.p.m. Samples for each refractometer reading were taken every few minutes at first, while crystallization was proceeding rapidly, but less often as the crystallization rate became slower. Calculations of the velocity constants were based on the integrated form of the Noyes and Whitney equation,

$$k = \frac{1}{0.4343 \sigma (\theta_2 - \theta_1)} \log \frac{c_1 - c_s}{c_2 - c_s} \quad (1-2)$$

σ was assumed to be constant and equal unity.

2. MODERN THEORIES OF CRYSTAL GROWTH.

Of the various theoretical treatments of this topic propounded from time to time the following have been given more detailed study and are listed with brief comment.

(A) SURFACE ENERGY THEORIES.

A thermodynamic approach was made by Gibbs⁴ and Curie⁵. An isolated droplet of fluid is in its most stable form when its surface free energy is a minimum. They therefore proposed that the shape of a growing crystal is the one with a minimum surface energy. However, such theories carry little weight in the present day.

(B) DIFFUSION THEORIES.

Noyes and Whitney⁶ proposed that a film of saturated solution is formed at the surface of solute and solvent. The velocity of solution would then be mainly dependent upon the diffusion gradient. They accepted that crystallization was the reverse of dissolution, and that both processes had rates of crystal growth which were determined by the concentration difference.

$$\text{For crystallization, } dM/d\theta = K_M \sigma (c - c_s) \quad (1-3)$$

Nernst⁷ postulated that the solute molecules would diffuse through a thin laminar film of liquid adjacent to the growing surface face. He thus modified the equation to

$$dM/d\theta = D/x (c - c_s) \quad (1-4)$$

Marc⁸ maintained that the concept of film diffusion was inadequate as the film thickness was negligible in strongly agitated conditions. He also demonstrated that crystallization is not necessarily the reverse of dissolution as a substance usually dissolves more rapidly than it crystallizes.

Berthoud⁹ and Valetton¹⁰ proposed that the diffusion process,

$$dM/d\theta = K_D \sigma (c - c_1) \quad (1-5)$$

is followed by a first-order reaction when solute molecules incorporate themselves into the crystal lattice,

$$dM/d\theta = K_r \sigma (c_1 - c_s) \quad (1-6)$$

However, the proposal of a first-order surface reaction is hardly warranted. It has been pointed out that many inorganic salts, crystallizing from aqueous solutions, show rates slightly greater than the first-order, while others indicate a ^{order} second-order reaction. Moreover, the value of the rate constant K_r changes from face to face on a crystal.

In practice c_i is removed by the use of an overall concentration driving force, $c - c_s$, and the reciprocal of the overall mass transfer coefficient is replaced by $(1/K_D + 1/K_r)$, yielding the equation,

$$dM/d\theta = \sigma(c - c_s) / (1/K_D + 1/K_r) \quad (1-7)$$

Thus for very rapid surface reaction $1/K_r$ is ignored, and the overall mass transfer coefficient becomes approximately K_D , implying that the process is directed by diffusion. Similarly, if the diffusional resistance is low, the overall mass transfer coefficient is approximately K_r , and the process is dominated by surface reaction.

Whitman's two-film theory has been helpful in the examination of mass transfer between two immiscible phases: however, it is generally felt that the film concept, which is the foundation of the theory of mass transfer, gives an over-simplified view.

The surface renewal theory as well as the film theory can be utilised in mass transfer operations other than gas absorption. The driving force for mass transfer is regarded as the concentration difference between the bulk of the fluid and the interface. In crystallization both theories can be expressed,

$$K_D = D/x \text{ (stagnant film)} \oplus \sqrt{Df} \text{ (random surface renewal)} \quad (1-8)$$

It is notable that so far there is no decisive evidence to help choose between the film and surface renewal theories.

(C) ADSORPTION LAYER THEORIES.

The concept of crystal growth being founded upon an adsorbed layer of solute atoms or molecules was propounded by Volmer¹¹ and others. Volmer showed that there was high mobility in the adsorbed state, and therefore the rate of growth will be dependent upon the rate at which the molecules strike the growing crystal surface and the concentration of the critical nuclei which can continue growing.

Volmer examined this situation for liquid droplets growing from vapour, and obtained ^{for} velocity of condensation,

$$k = N^{3/2} 4\pi r^*{}^2 \psi / \sqrt{2\pi MRT} e^{-4/3 \pi r^*{}^2 N/RT} \quad (1-9)$$

Becker and Doring¹², looking at the phenomenon from kinetics rather than thermodynamics, secured the result given by Frenkel¹³ and others,

$$k = N^2 2\pi r^*{}^2 \psi / RT \sqrt{1/3 [(v_g - v_l)/M] m^*} \quad (1-10)$$

It appears that the main forms of these growth equations are in agreement with experimental results.

In condensed systems, the collisional factor means that there must be transport by molecular diffusion. Becker postulates that the nucleation rate,

$$J = C e^{-v/RT} N e^{-A(T)/RT} N \quad (1-11)$$

If these nuclei are spherical, velocity of crystallization,

$$\begin{aligned} k &= C e^{-N/RT} (v - 4/3 \pi r^*{}^2) \\ &= C e^{-N/RT} [v + 4/3 \pi r (2v_l T / \lambda \{T_0 - T\})^2] \end{aligned} \quad (1-12)$$

utilising the Gibbs-Thomson and Clapeyron-Clausius equations.

Since $e^{-vN/RT}$ decreases with decreasing temperature or increasing supersaturation, while $e^{-A(T)N/RT}$ acts in a converse manner, the rate curves for both nucleation and growth will attain maxima.

For the discrepancy between theory and practice for the rate of growth of a crystal at low supersaturations, an explanation was propounded by Frank¹⁴. He put forward that, when a crystal contained a dislocation which was self-maintaining, the necessity for surface nucleation would be prevented to a great extent, and the crystal would grow continuously even at very low supersaturations.

The proposal was followed by ardent search for such dislocations. They have been discovered in almost every case where there has been thorough examination. Hence it may be concluded from growth and evaporation studies that a dislocation mechanism is very possible.

One kind of defect is screw dislocation. During the process of crystal growth, a step may appear on the crystal face. When a screw dislocation has taken place, then the crystal face continues to grow "up a spiral staircase." Thus the Adsorption Layer Theory shows how a crystal can be formed, and how imperfections in crystals can be brought about.

3. THE GROWTH RATE AND CONCENTRATION.

Kucharenko's values for the crystallization of sucrose from pure solutions have been recommended by the I.C.U.M.S.A.¹⁵ as tentative standards until they have been confirmed and extended.

Van Hook¹⁶, using Kucharenko's smoothed values, plotted crystallization velocity v . oversaturation (% basis). He states that the curves exhibit a pronounced curvature which would be considerably reduced if the supersaturation were expressed in some sort of a ratio concentration such as sugar/water ratio. He maintains that the approach to linearity suggests a growth equation of the form,

$$V / (S - 1) = \text{constant} \quad (1-13)$$

Kucharenko's results have received a certain amount of confirmation. Van Hook¹⁶ and his co-workers have gained similar figures at 20°, 30° and 40°, but their results at higher temperatures drop behind those of Kucharenko.

Several explanations have been given concerning increasing crystallizing potential. Three of these are as follows:-

(1) Strain increases growth. Van Hook¹⁶ and his fellow workers have shown that the rate of growth can be increased by 50% by thermal shock.

(2) The rate of crystallization changes considerably from one crystal to another. Bjerager¹⁷ demonstrated this by photomicrographs of growing crystals and attributed the differences to changes in crystal habit.

(3) When crystals grow rapidly, more heat is produced per unit time. If this heat is not completely dissipated and the influence of increasing temperature on the reaction velocity is stronger than on solubility, the crystallization velocity will increase.

4. THE GROWTH RATE AND STIRRING.

The crystal rate of growth at a certain temperature under constant conditions of supersaturation can be influenced by agitation. The rate* is appreciable in the early stages since the relative velocity between the crystal and liquid is increased, but the position is rapidly attained where agitation ceases to influence the growth rate.

For crystal growth in a supersaturated solution under a constant concentration driving force, the rate of mass transfer,

$$k = f(\mu, \rho, v, D, d) \quad (1-14)$$

$$\text{Hence } kd/D = C (\rho vd/\mu)^a (\mu/\rho D)^b \quad (1-15)$$

where the groups $\rho vd/\mu$, $\mu/\rho D$ and kd/D are the dimensionless Reynolds (Re), Schmidt (Sc) and Sherwood (Sh) numbers.

The reaction rate is usually regarded as the power function of the rate of stirring,

$$k = \alpha I^\beta \quad (1-16)$$

where β approaches unity when reaction is diffusion controlled, but under normal conditions is 0.25 or less.

Zubchenko¹⁸ reported that increasing the stirring speed assisted in the formation of finer crystals and less coarse crystals, and to a small increase in growth.

* "is appreciable in the early stages since" is better "increases considerably in the initial stages as"

5. THE GROWTH RATE AND IMPURITIES.

When there is an additional component in a solution of sucrose, and sucrose is the solute with which we are mainly concerned, the solution is regarded as 'impure' in relation to sucrose. It is generally true that impurities will hinder the velocity of crystallization of sucrose.

Kucharenko¹⁹ has demonstrated that the presence of caramel retards the velocity of crystallization of sucrose at 50°. He has also shown that the presence of lime retards the velocity of crystallization of sucrose at 30° and 50°. He found in the cases of 0.5%, 1% and 2% of CaCl_2 at 50° that there was a critical oversaturation (approximately 1.03), that with concentrations above this critical oversaturation, CaCl_2 decreased the sucrose crystallization velocity; while with concentrations below this critical oversaturation, CaCl_2 increased the crystallization rate.

Yamaguchi, Imazeki and Kaneyuki²⁰ found that CoCl_2 retarded crystallization and reduced the crystal yield; and amarinth retarded crystallization, without influencing the crystal yield.

Sucrose crystallization in the presence of raffinose has been examined by Mantovani and Fagioli²¹. Raffinose had a very *little salting-out effect on sucrose solubility and increased the viscosity slightly. They concluded that raffinose was adsorbed on the growing crystal surface and hindered crystal growth, ultimately being caught slightly in the crystal.

6. THE PLACE OF VISCOSITY IN CRYSTAL GROWTH.

If viscosity controls sucrose crystallization, there must be growth by diffusion. The Stokes-Einstein equation shows that the two are reciprocal. However, strong sugar solutions show a certain variance on this.

Van Hook²² has compared the energies of activation of viscosity, diffusion and growth, concluding that the former two

are much less than the third over the usual temperature range. The comparison was carried out at constant supersaturation of 1.05. It was only at high temperatures that the three curves approached a common low level. Van Hook concluded that the transport step is not decisive at low temperatures, but that it becomes important at higher temperatures. Nees and Hungerford²³ and Orth²⁴ have also stressed that viscosity appears to be only a secondary factor in the rate equations.

However, most give viscosity a significant part in sucrose crystallization. The observations of Smythe² substantiate the conclusions of Vernon²⁵ that the diffusion process is a vital factor in determining the rate of crystallization of sucrose. At low temperatures the limitation to the rate of crystallization brought about by the diffusion of molecules to and from the crystal surface can be reduced to a minimum by increasing the relative motion of the crystal and solution. At high temperatures it is exceedingly hard to reach velocities high enough to overcome this influence.

The evidence suggests that when diffusion is a vital factor in determining the rate of crystallization, the order of the process is greater than one. It is notable that the activation energies obtained by Smythe are very similar to those for processes controlling the viscosity of sucrose solutions in this temperature and concentration range. While below 50°, these values are much higher than those for diffusion, above 50° the activation energies of viscosity and rate of crystallization tend towards that of diffusion.

Pryor and Roscoe²⁶, Skiiio²⁷ and others have attributed the anomalous relationship between viscosity and diffusion to the hydration of sucrose in aqueous solutions. They demonstrated that the hydration of sucrose decreases from approximately 0.6 mole H₂O per ^{-OH} group of sucrose at 20° to approximately 0.1 mole H₂O per -OH group at 70°. In temperatures 20° to 45°, Skiiio

found that the enthalpy change of hydration of sucrose was about 13 k.cal/mole. This is of the order of magnitude of the energy of H bonding in sucrose and very close to the activation energies for growth, ~~and~~ nucleation and viscosity of sucrose solutions. Hence the solution can be considered as hydrated molecules dissolved in the remaining free water. The increase in activation energy of viscosity with increasing concentration can be attributed to increasing hydration and the production of larger particles. In the same way, the decrease in activation energy of viscosity at higher temperatures can be attributed to decreasing hydration and the tendency to greater direction of viscosity by the diffusion process.

Smythe² therefore proposed that both viscosity and the crystallization rate are directed by the same process with two main rate-controlling steps: (1) diffusion and (2) hydration of the sucrose molecule. The activation energy of the rate of crystallization at lower temperatures where diffusion influence is at a minimum, tends to the energy needed for the dissociation of the sucrose-water complex.

Dunning and Shipman²⁸ determined a value of approximately 16 k.cal/mole for the activation energy of the process of nucleation in sucrose solutions in the temperature range 0-40°. Smythe² maintains that since this is close to the activation energies for crystal growth and viscosity, it suggests that the processes governing these three phenomena are essentially the same. At higher temperatures, diffusion plays an increasingly vital part in these three processes, and their activation energies approach that of diffusion.

7. CRYSTALLIZATION AND DISSOLUTION.

Most maintain that in the crystallization process after diffusion there is a subsequent surface reaction at the growing crystal face. Some consider that crystal dissolution is speedier than growth as the exposed solid surfaces are not

identical. When a crystal grows the faces are plane, but when it dissolves the faces are often pitted which means a larger solid-liquid contact. Emmerich and Forth²⁹ measured the crystallization rates of small crystals at $S = 1.00-1.03$ at 20° . Changes in the initial values of the rate were revealed as caused by crystal surface imperfections. Pounded crystals with great defects had initial rates over 10 times the normal value.

Kucharenko¹ measured the rate of dissolution of sucrose crystals in near saturated solutions at 60° . Van Hook³⁰ found from Kucharenko's data that solution velocities were 5 or more times the crystallization rate at equal displacements from saturation.

Surface pitting can increase the rate of mass transfer in dissolution, but there could also be a time-taking surface reaction during crystallization. Van Hook³⁰ maintains that a high assessment of additional surface area owing to pitting, cannot explain the greater rate of solution compared with the crystallization rate under similar conditions.

8. THE HEAT OF CRYSTALLIZATION.

Kaganov and Zhigalov³¹, using Kucharenko's experimental data, found the special crystal growth rate by plotting growth rate (mm/hr) v. sucrose concentration (expressed in three ways as g/g, molarity and molality) (30° , 40° , ... 70°), and calculating values of the crystallization temperature coefficient. They then plotted the logarithm of the special growth rate against $1/T$ to demonstrate the validity of the Arrhenius formula at $30^\circ-70^\circ$. The crystallization process was shown by them to be made up of two distinct zones; the diffusion zone where activation energy had a maximum of 7 k.cal, and the kinetic zone, where the activation energy was at least 10 k.cal. The linear crystal growth rate was given by

$$k = 2.42 \times 10^5 e^{-8,780/RT} \Delta S_u \quad (1-17)$$

If the sucrose:water ratio was used, the coefficient was 9.73×10^5 .

The heat of crystallization and heat of solution are usually regarded as synonymous and the values normally recorded in handbooks for the heat of solution refer to this value "as at infinite dilution". While these values may have certain applications, it is thought that for the study of the actual heat of crystallization we are more especially concerned with the "last heat of solution." This is essentially the heat effect of the last molecule going in to solution as it approaches saturation.

Lyle³² studied calorimetrically actual crystallization and solution heat effects, and rationalised his data into the following equation,

$$Q_{s_1 s_2 t} = -50/9 \{2 - 153/(9+s_1)(9+s_2)\} - 19/40 (258+t)t/1000 \text{ cal/g. sucrose (1-18)}$$

This is an empirical equation and its chief value is that it can be used to calculate actual values for these heat effects at concentration conditions of real interest in crystallization studies.

From the more theoretical point of view we might consider certain analogies between the heat of crystallization from saturated solutions and the latent heat of vapourisation for vapour-liquid systems. For this purpose the classical Clapeyron-Clausius treatment of vapour-liquid systems is transferred by analogy to the study of solution-solute equilibrium relationships. This gives the following equation,


$$\log_e c_1/c_2 = \Delta H/R (T_1 - T_2)/T_1 T_2 \quad (1-19)$$

As with the latent heat values the heat of crystallization so calculated is a temperature dependent function which from the study of numerous solubility data seems generally to be able to

be expressed as

$$Q = \alpha + \beta T$$

(1-20)



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CHAPTER 2. VISCOSITY CHARACTERISTICS OF THE
SUCROSE - ETHANOL - WATER SYSTEM.

1. INTRODUCTION.

Experimental data on the solubility of sucrose in aqueous ethanol solutions¹ showed that sucrose solubility decreased as the ethanol content of the solvent increased. Since the viscosity of pure sucrose solutions diminishes with the lowering of sucrose concentration, it was possible that the viscosity of solutions, saturated with respect to sucrose, would decrease with increase of ethanol concentration in the solvent. Thus a series of experiments was carried out with the purpose of determining the actual viscosity values for these saturated solutions, and the results are recorded in this chapter. The rate of change of the viscosity of a solution with temperature was also examined, and the results are interpreted and discussed in terms of energy values.

The solubility values for sucrose in aqueous ethanol solutions used in these studies are set out in Table 2-1.

Table 2-1. SOLUBILITY OF SUCROSE IN AQUEOUS ETHANOL.

<u>Mass Fraction of Water</u>	<u>Solubility g/g. solvent</u>			<u>Solubility g/g water</u>			<u>Solubility Coefficient</u>		
	<u>20°</u>	<u>30°</u>	<u>40°</u>	<u>20°</u>	<u>30°</u>	<u>40°</u>	<u>20°</u>	<u>30°</u>	<u>40°</u>
1.0	2.02	2.17	2.36	2.02	2.17	2.36	1.0	1.0	1.0
0.9	1.72	1.87	2.12	1.91	2.08	2.36	0.95	0.96	1.0
0.8	1.48	1.58	1.78	1.85	1.98	2.22	*0.87	0.91	0.95
0.7	1.16	1.28	1.50	1.66	1.83	2.14	0.82	0.84	0.91
0.6	0.88	0.99	1.22	1.47	1.65	2.03	0.73	0.76	0.86
0.5	0.61	0.70	0.92	1.22	1.40	1.84	0.60	0.65	0.78

* 0.92

The values in Table 2-1 include the solubility coefficient which reveals the degree of departure from the solubility of sucrose in water. For these studies solubility coefficient is defined as the ratio of the molal concentration of sucrose in aqueous ethanol (with respect to the sucrose-water constituents) to the solubility of sucrose in water. Of the many values for the solubility of sucrose in water², those secured by Kelly³ have been preferred as a basis for the current studies. Variations in published values of aqueous sucrose solubilities are discussed in greater detail in chapter 4.

2. EXPERIMENTAL.

A Hoespler Viscometer was used to determine absolute viscosities. This is a precision instrument of established acceptance in this field. It consists of an inclined glass tube which is enclosed in a water jacket. Suitably calibrated balls are allowed to roll down the side of the tube which has three guage markings, and a stopwatch used for ascertaining the rate of movement of a ball through a specified distance of the solution being studied. These times varied from 15.2 to 133.9 seconds.

This Viscometer proved to be very satisfactory for clear solutions. However, the presence of even small amounts of minute particles in suspension and on the side of the tube tended to retard the rate of motion of the ball. This appeared to occur in the present studies when solutions were supersaturated with respect to sucrose and had fairly high viscosities (about 2 poises and over). Although a small number of nuclei present in these solutions might only have a very slight effect on the concentration or true viscosity, the observed rate of motion of the ball in the inclined tube was far less consistent than in the case of unsaturated solutions.

It was therefore decided in these circumstances to adjust the Viscometer tube to bring it into a vertical position in order

to reduce the effect of minute crystals on the rate of the ball. Results with a satisfactory high degree of consistency were then secured. Viscosities at 20° of pure sucrose solutions saturated at 20°, 30° and 40° were 222.0, 319.4 and 513.6 cP respectively. Values obtained from polynomials applied to tabulated values were 220.9, 320.9 and 515.1 cP respectively.

Truly spherical glass or steel balls were used to cover the range of viscosities studied (up to 513.6 cP), and each was suitably calibrated. The viscosities of aqueous sucrose solutions are known with a high degree of precision⁴, and these were used for the purpose of calibration.

The equation provided with the instrument for the calculation of viscosity values was,

$$\mu = \theta \times (\rho_b - \rho_1) \times C_b \quad (2-1)$$

The data concerning ball constants for the Viscometer is set out in Table 2-2.

Table 2-2. BALL CONSTANTS.

<u>Ball</u>	<u>Normal Position</u>		<u>Vertical Tube</u>	
	<u>Constant</u>	<u>Range (cP)</u>	<u>Constant</u>	<u>Range (cP)</u>
Glass I	0.07537	0 - 30		
Glass II	0.7602	30 - 300	0.8490	180 - 300
Metal	0.9531	180 - 600	1.028	200 - 600

At least duplicate measurements were made at each condition studied. (in order to obtain the highest possible precision) The results are recorded in Table 2-3, together with the viscosities of saturated aqueous sucrose solutions. The viscosities of these latter solutions were extrapolated from the tabular values⁴, using a second order polynomial equation over three concentration steps, each one percent apart at the temperature of study (See Table 2-5).

* Omit (.....)

Table 2-3. VISCOSITY VALUES. (x means extrapolated values)

<u>Mass Fraction of Water</u>	<u>Saturation Temperature</u> °	<u>Solution Composition</u> (per weight percent)			<u>Temp.</u> °	<u>Viscos.</u> cP
		<u>Sucrose</u>	<u>Ethanol</u>	<u>Water</u>		
1.0	20	66.89	0	33.11	20.0	222.0
1.0	20	66.89	0	33.11	30.2	104.1
1.0	20	66.89	0	33.11	40.25	58.7
1.0	30	68.45	0	31.55	20.0	319.4
1.0	30	68.45	0	31.55	30.0	149.5
1.0	30	68.45	0	31.55	40.15	80.7
1.0	40	70.25	0	29.75	20.0	513.6
1.0	40	70.25	0	29.75	30.0	220.7
1.0	40	70.25	0	29.75	39.9	117.3
1.0	50	72.19	0	27.81	50	x100.3
1.0	55	73.22	0	26.78	55	x93.9
1.0	60	74.28	0	25.72	60	x89.4
1.0	65	75.35	0	24.65	65	x85.8
0.9	20	63.24	3.676	33.084	20.0	163.6
0.9	20	63.24	3.676	33.084	29.9	82.6
0.9	20	63.24	3.676	33.084	40.0	46.7
0.9	30	65.16	3.484	31.356	20.0	233.5
0.9	30	65.16	3.484	31.356	30.0	114.7
0.9	30	65.16	3.484	31.356	40.15	61.7
0.9	40	67.95	3.205	28.845	20.0	445.9
0.9	40	67.95	3.205	28.845	30.2	201.7
0.9	40	67.95	3.205	28.845	40.0	105.5
0.8	30	61.23	7.754	31.016	30.0	82.0
0.8	40	64.03	7.194	28.776	40.0	61.4
0.8	45	65.90	6.82	27.28	45.0	72.75

Table 2-3. VISCOSITY VALUES (cont'd).

<u>Mass Fr.</u> <u>of Water</u>	<u>Saturation</u> <u>Temp. °</u>	<u>Solution Composition</u>			<u>Temp.</u> <u>°</u>	<u>Viscosity</u> <u>cP</u>
		<u>Sucrose</u>	<u>Ethanol</u>	<u>Water</u>		
0.7	20	53.71	13.887	32.403	20.0	71.00
0.7	20	53.71	13.887	32.403	30.0	38.34
0.7	20	53.71	13.887	32.403	40.1	22.32
0.7	30	56.14	13.158	30.702	20.0	101.00
0.7	30	56.14	13.158	30.702	30.0	52.53
0.7	30	56.14	13.158	30.702	40.0	29.82
0.7	40	60.00	12.000	28.000	20.0	186.3
0.7	40	60.00	12.000	28.000	30.1	94.53
0.7	40	60.00	12.000	28.000	40.0	51.89
0.5	20	37.88	31.060	31.060	20.0	19.15
0.5	20	37.88	31.060	31.060	29.9	11.86
0.5	20	37.88	31.060	31.060	40.0	7.75
0.5	30	41.15	29.425	29.425	20.0	25.71
0.5	30	41.15	29.425	29.425	30.0	15.41
0.5	30	41.15	29.425	29.425	40.0	9.69
0.5	40	47.92	26.040	26.040	20.0	55.69
0.5	40	47.92	26.040	26.040	30.1	30.34
0.5	40	47.92	26.040	26.040	40.0	18.44

Owing to limitations of time, it was decided to only carry out extensive viscosity experiments at the temperatures 20°, 30° and 40°. Viscosity determinations were effected for each solution at these temperatures, and the viscosity at saturation was suitably interpolated. Not only did this technique prove to be satisfactory for this purpose, but it was also valuable for determining the rate of change of viscosity of a particular solution with temperature, as will be discussed later in this chapter.

3. GRAPHICAL ANALYSIS OF VISCOSITY DATA.

Figure 2-1 illustrates the Viscosity - Temperature relationship for aqueous sucrose solutions, covering a wider range of temperatures than those used for the current studies. The data used for this graph are as follows:-

- (1) Values measured in these studies; and
- (2) Extrapolated values calculated from constants calculated from polynomial treatment of tabulated values⁴.

Appropriate marking is used to indicate the two sources of information. The main purpose of this plot is to show that there is a minimum value for the viscosity (calculated as 80.2 cP) of a saturated aqueous sucrose solution at a temperature of 82.5° and a concentration of 79.025% sucrose. *

The existence of such a minimum viscosity appears to have been first pointed out by Micheli and de Gyulay⁵ in a study of the viscosity of naturally occurring cane sugar syrups at saturation conditions. Further investigation in this field was carried out by Kelly and McAntee⁶. In each case it was evident that the temperature of the minimum viscosity at saturation decreased progressively as the concentration of non-sucrose solute increased. It was considered that such might also well be the case in the sucrose - aqueous ethanol system, and the data illustrated in Figures 2-2, 2-3 and 2-4 show that this is correct. In Figure 2-5 is illustrated the derived relationship between minimum viscosity of a saturated solution and solvent composition, and in Figure 2-6 the derived relationship between temperature of a saturated solution and solvent composition.

* Payne^{4A} places the minimum at 70° and 84 cP, according to the solubility selected.

Figure 2-1. VISCOSITY V. TEMPERATURE
1.0 MASS FRACTION OF WATER IN SOLVENT

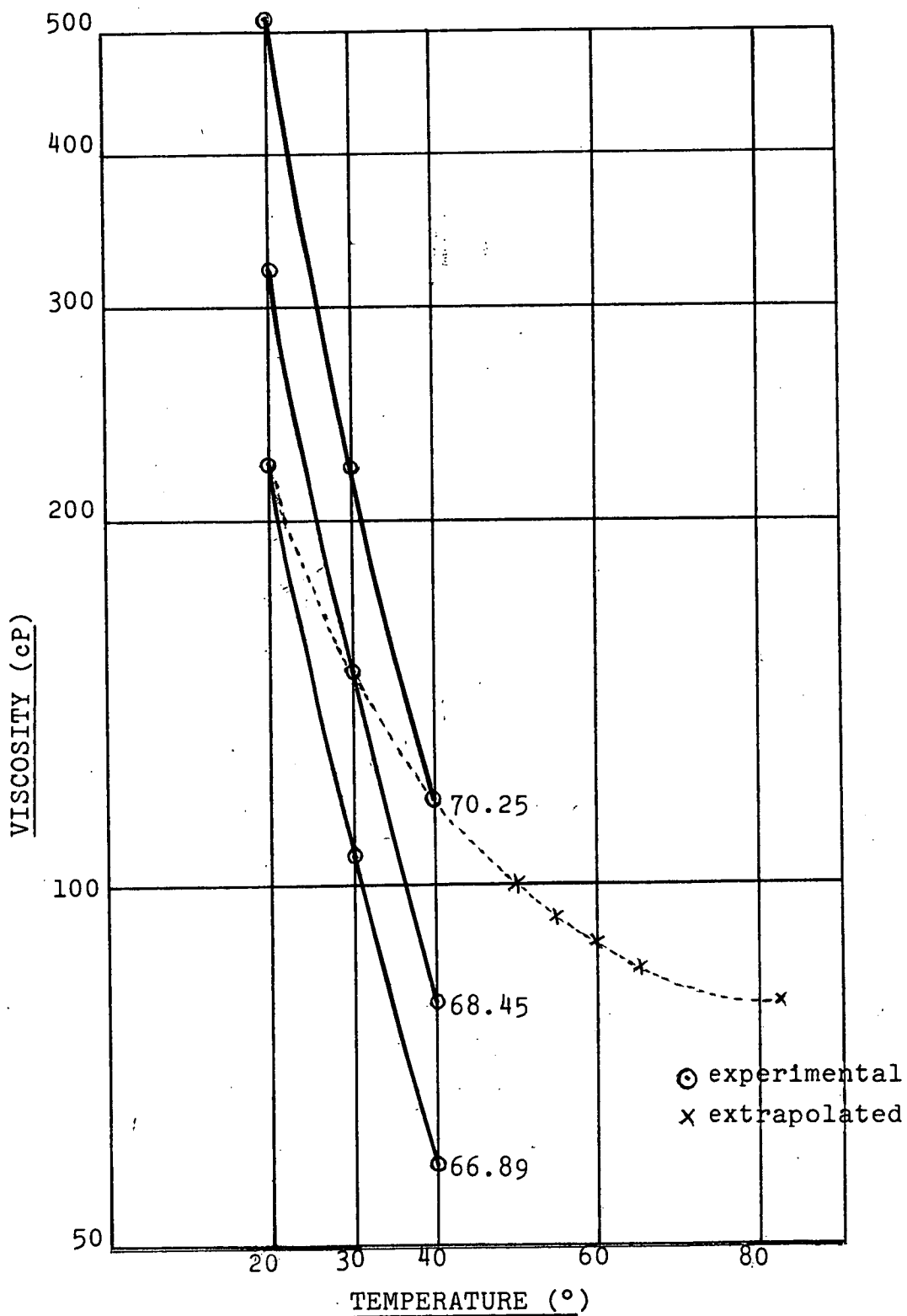


Figure 2-2. VISCOSITY V. TEMPERATURE
0.9 MASS FRACTION OF WATER IN SOLVENT

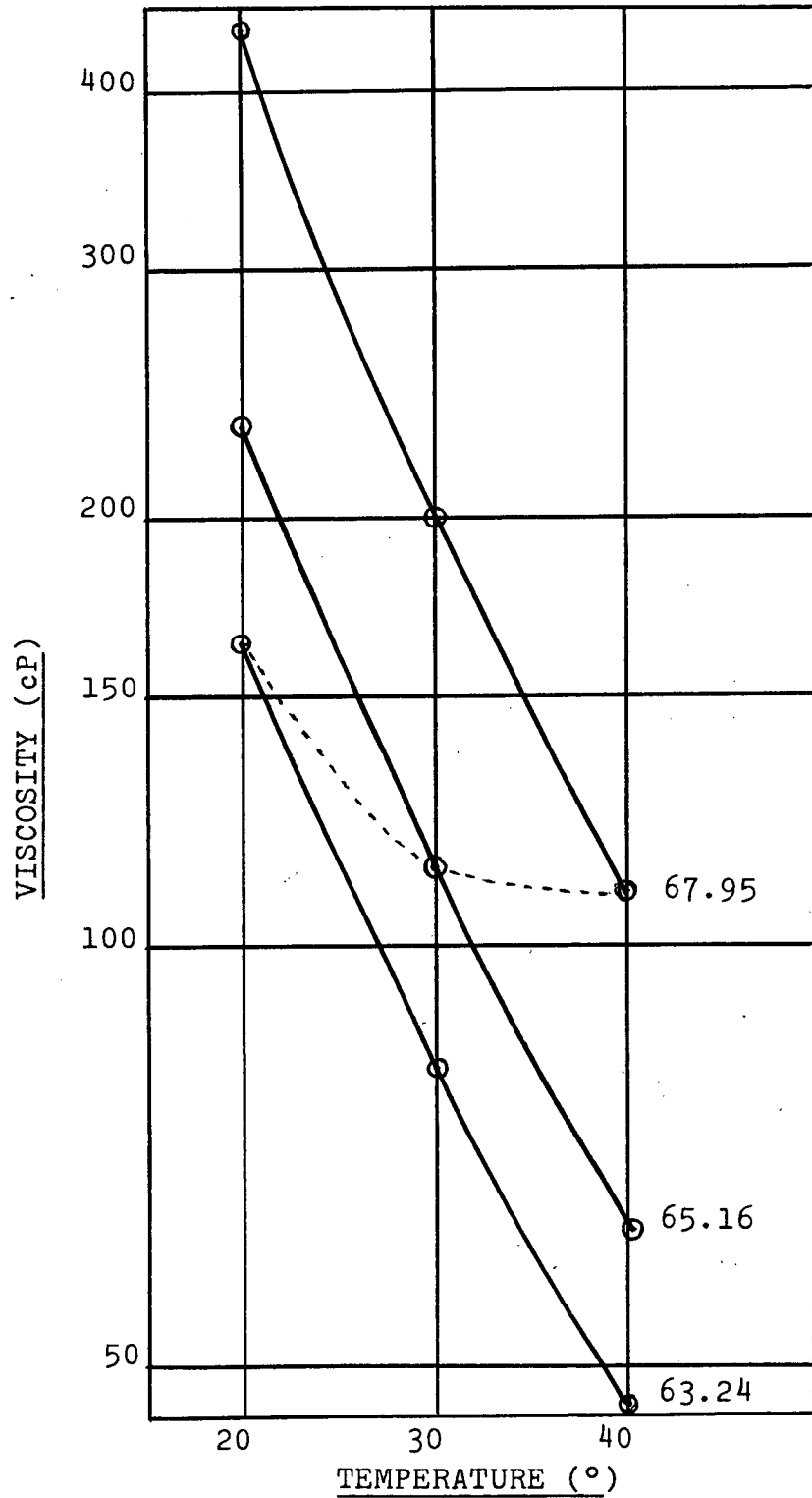


Figure 2-3. VISCOSITY V. TEMPERATURE
0.7 MASS FRACTION OF WATER IN SOLVENT

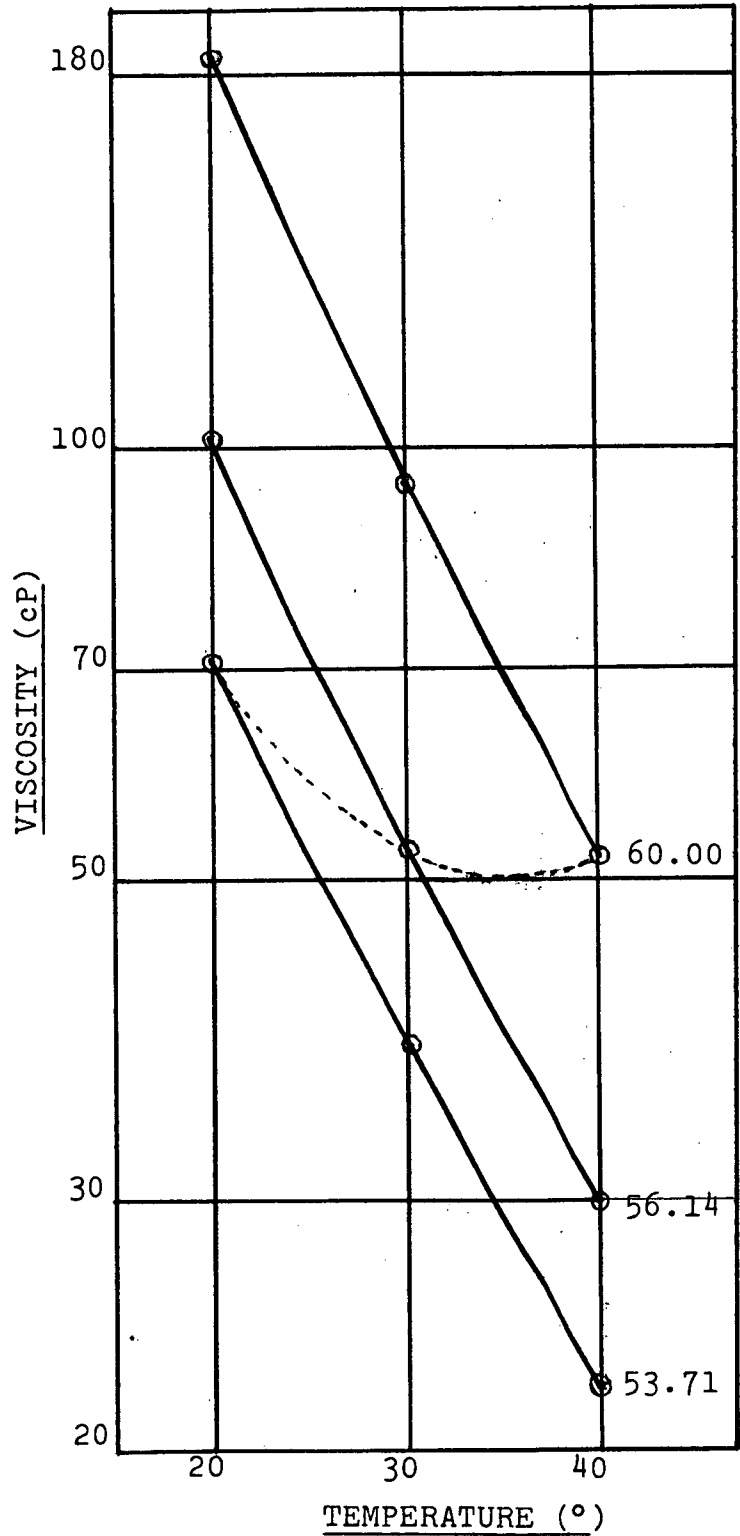


Figure 2-4. VISCOSITY V. TEMPERATURE
0.5 MASS FRACTION OF WATER IN SOLVENT

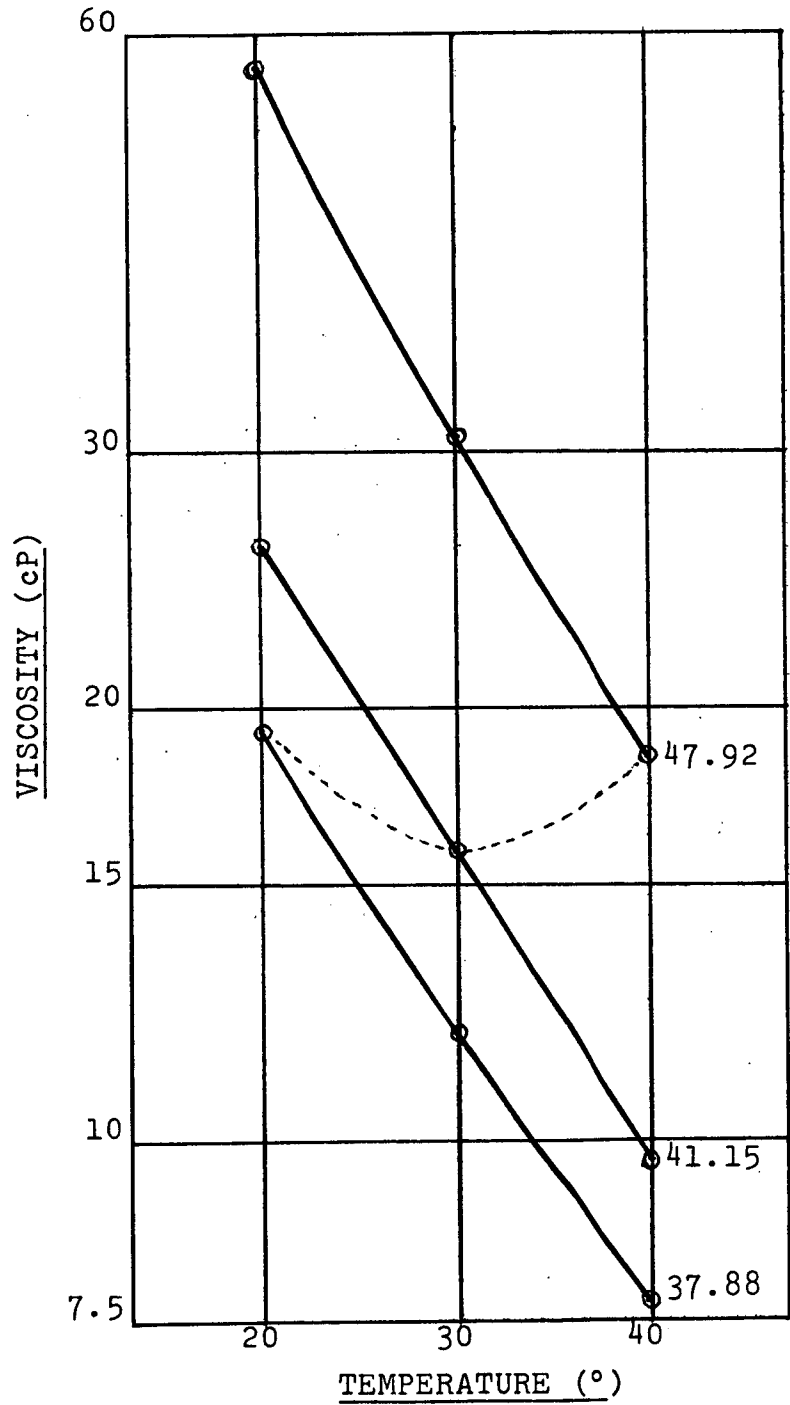


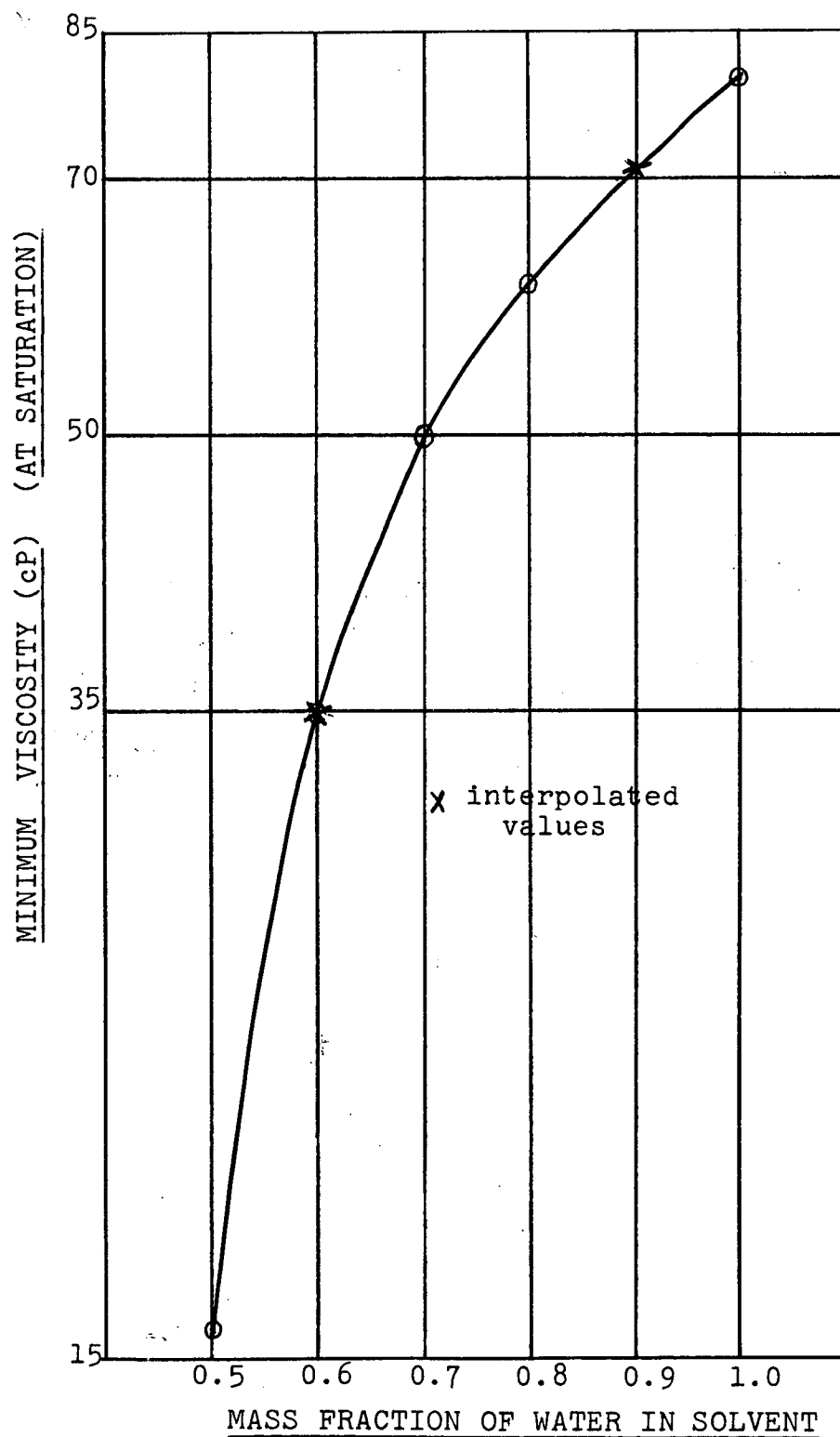
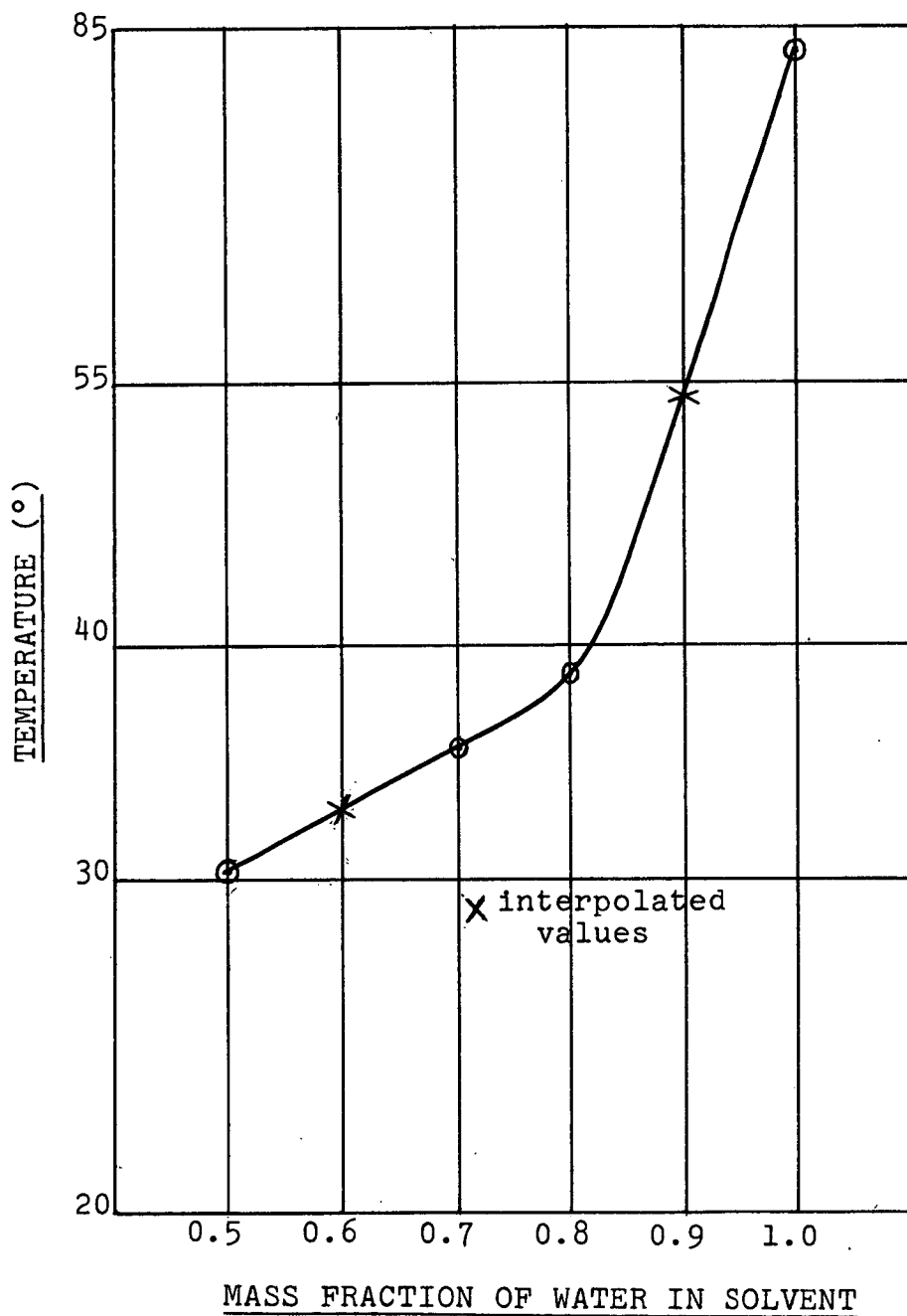
Figure 2-5. MINIMUM VISCOSITY (AT SATURATION)V. MASS FRACTION OF WATER IN SOLVENT

Figure 2-6. TEMPERATURE (AT MINIMUM VISCOSITY)
V. MASS FRACTION OF WATER IN SOLVENT



4. ENERGY CALCULATIONS FROM VISCOSITY - TEMPERATURE RELATIONSHIPS.

Van Hook⁷ studied the temperature coefficients at saturation of viscosity, diffusion and crystallization systems for aqueous sucrose in order to compare energy values. Probably because of study at low temperatures, he does not appear to have *considered the possible existence of a minimum value, at least in the viscosity relationship. Actually owing to similarity of system behaviour, the relative energy values thus calculated are probably not seriously in error.

However, in the current studies it was decided to avoid the problem of a minimum value now that its existence is well substantiated. Thus the viscosity - temperature relationships of solutions of specific concentrations were studied in terms of an Arrhenius relationship arranged as follows:-

$$\mu = P e^{A/RT} \quad (2-2)$$

It is well known that semi-log plots between viscosity and reciprocal absolute temperatures do not give a truly linear relationship in most systems. Kelly and McAntee⁶ indicated that this is true of aqueous sucrose solutions and those with non-sucrose solutes normally occurring in natural sugar cane syrups. Various methods have been used by workers in this field in an attempt to rationalise this observation.

In their studies, Kelly and McAntee adopted the proposal of Irani⁸ in which a pseudo-log scale is used for securing a straight line for one particular solution in the series and all the other solutions behave similarly unless some non-Newtonian abnormality develops. This technique is essentially graphical, and while probably giving an indication of even small departures from true Newtonian behaviour, it is valueless for rigorous mathematical analysis.

A second approach is one which was suggested by Gutmann and Simmons⁹, using a modified Arrhenius relationship of the following form,

$$\mu = P e^{A/R(T+\theta)} \quad (2-3)$$

This appears to be effective for graphically "rectifying" data in this system, but the determination of ϕ is tedious and is really a process of successive approximations. While the work might be facilitated by writing a suitable computer programme, it was decided for the purpose of the current study, that there were too many difficulties in finding an acceptable physico-chemical meaning for ϕ .

However, it may be noted that, by putting equation (2-2) in logarithmic form as in equation (2-4), a very close approximation to linearity over the logarithmic range of interest is obtained by means of a plot of $RT \log_e \mu$ against T .

$$RT \log_e \mu = A + BT \quad (2-4)$$

The systems studied have been plotted with these co-ordinates in Figures 2-7, 2-8, 2-9 and 2-10. In each case values for B (slope) = temperature coefficient and A (anti-log of intercept) have been calculated.

This information is presented in Table 2-4 together with added values for aqueous ethanol solutions of 0.8 and 0.6 mass fractions of water in solvent. Interpolations were made analytically by using a second order polynomial equation which appeared to fit the data very well over the range of conditions being studied (See Table 2-5).

A value has also been calculated for the standard deviation of observed values from the value obtained by using the recorded constants in equation (2-4). In this Table St.D., $\pm \sqrt{\Sigma(y_{\text{obs}} - y_{\text{calc}})^2 / m}$, is expressed as a percentage of the calculated value. The highest standard deviation (0.73% of calculated value) was that of the aqueous sucrose solution at 40°.

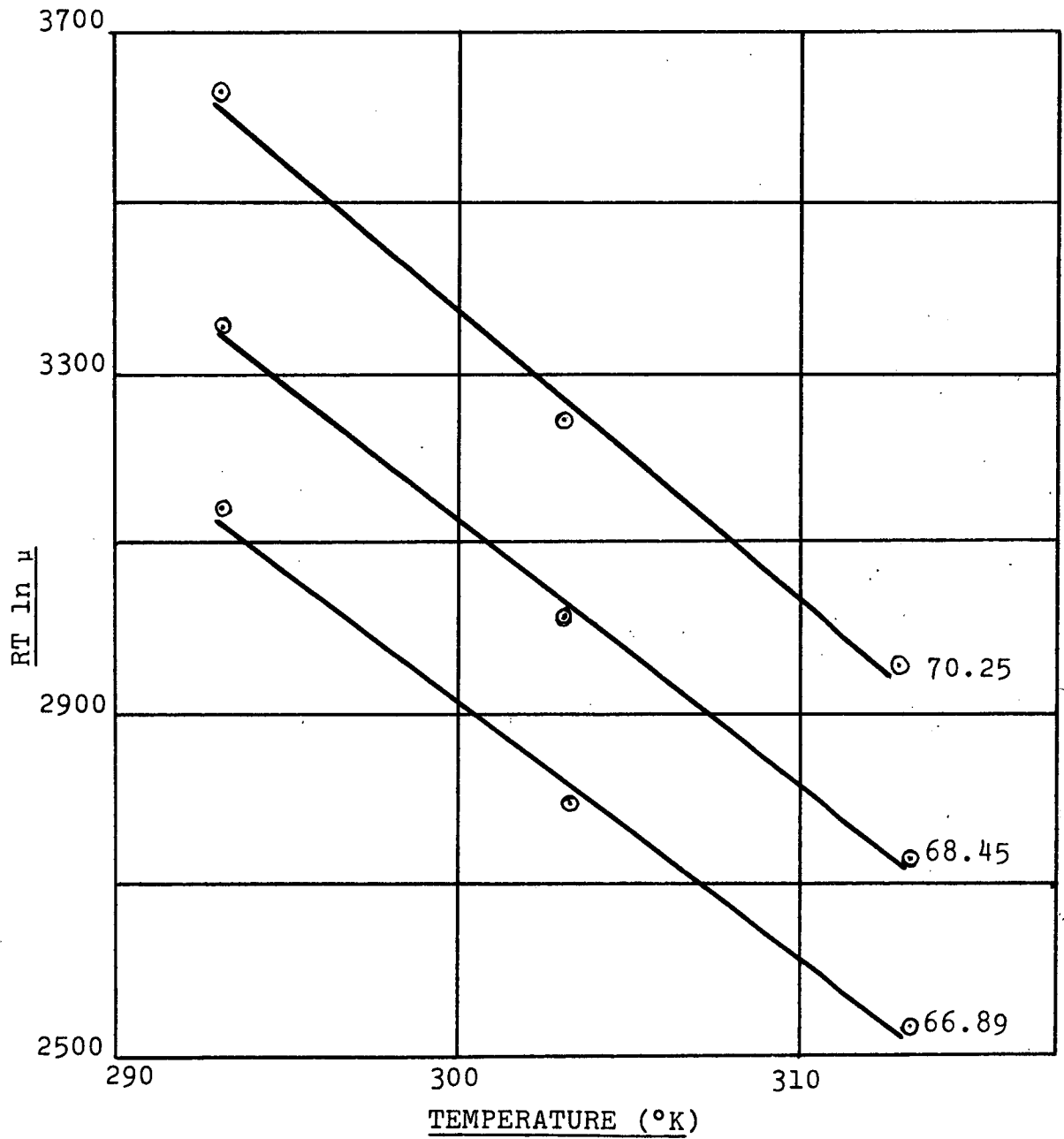
Figure 2-7. $RT \log_e \mu$ V. T 1.0 MASS FRACTION OF WATER IN SOLVENT

Figure 2-8. $\frac{RT \ln \mu}{V \cdot T}$
0.9 MASS FRACTION OF WATER IN SOLVENT

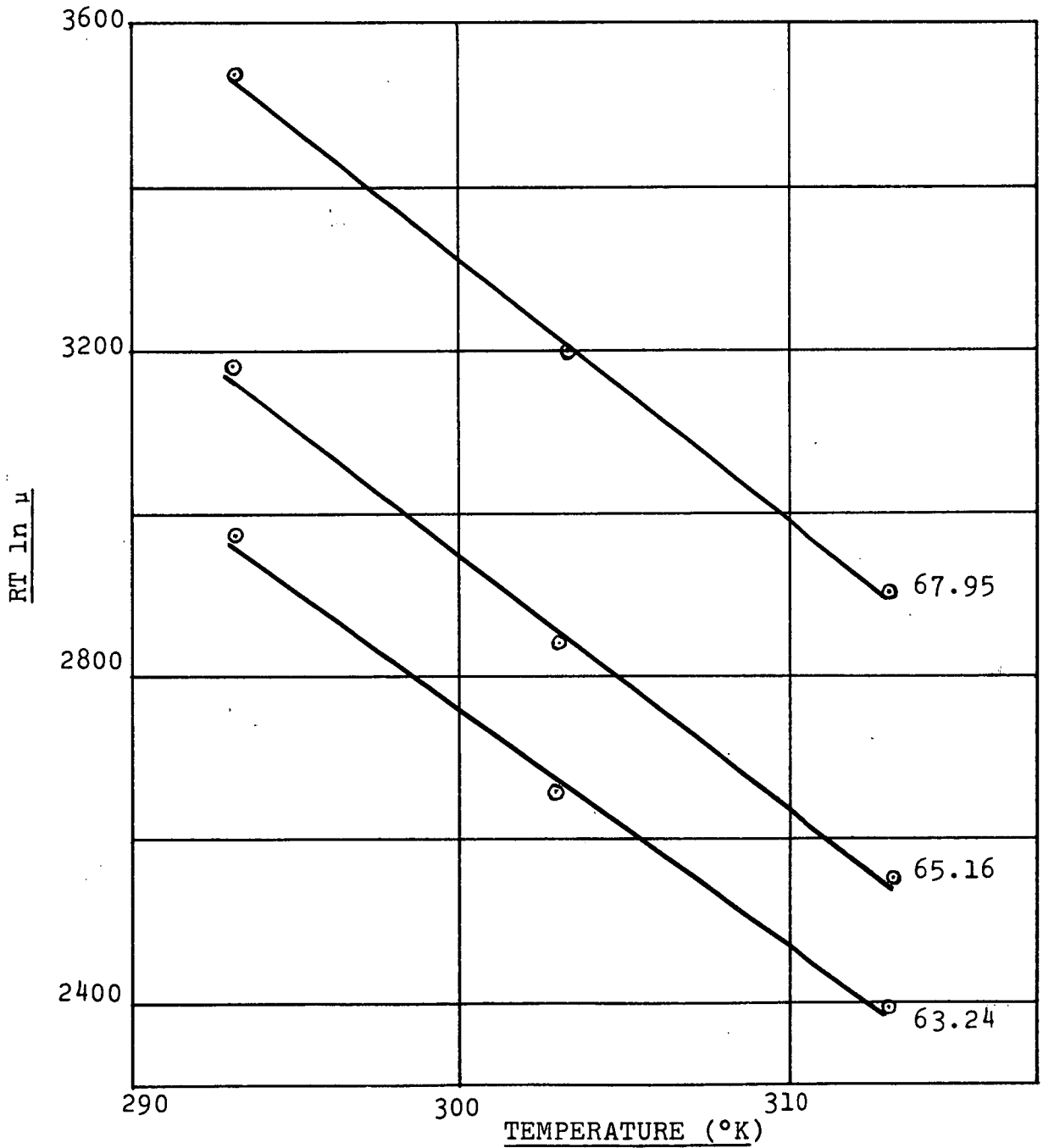


Figure 2-9. $RT \ln \mu$ V. T
0.7 MASS FRACTION OF WATER IN SOLVENT

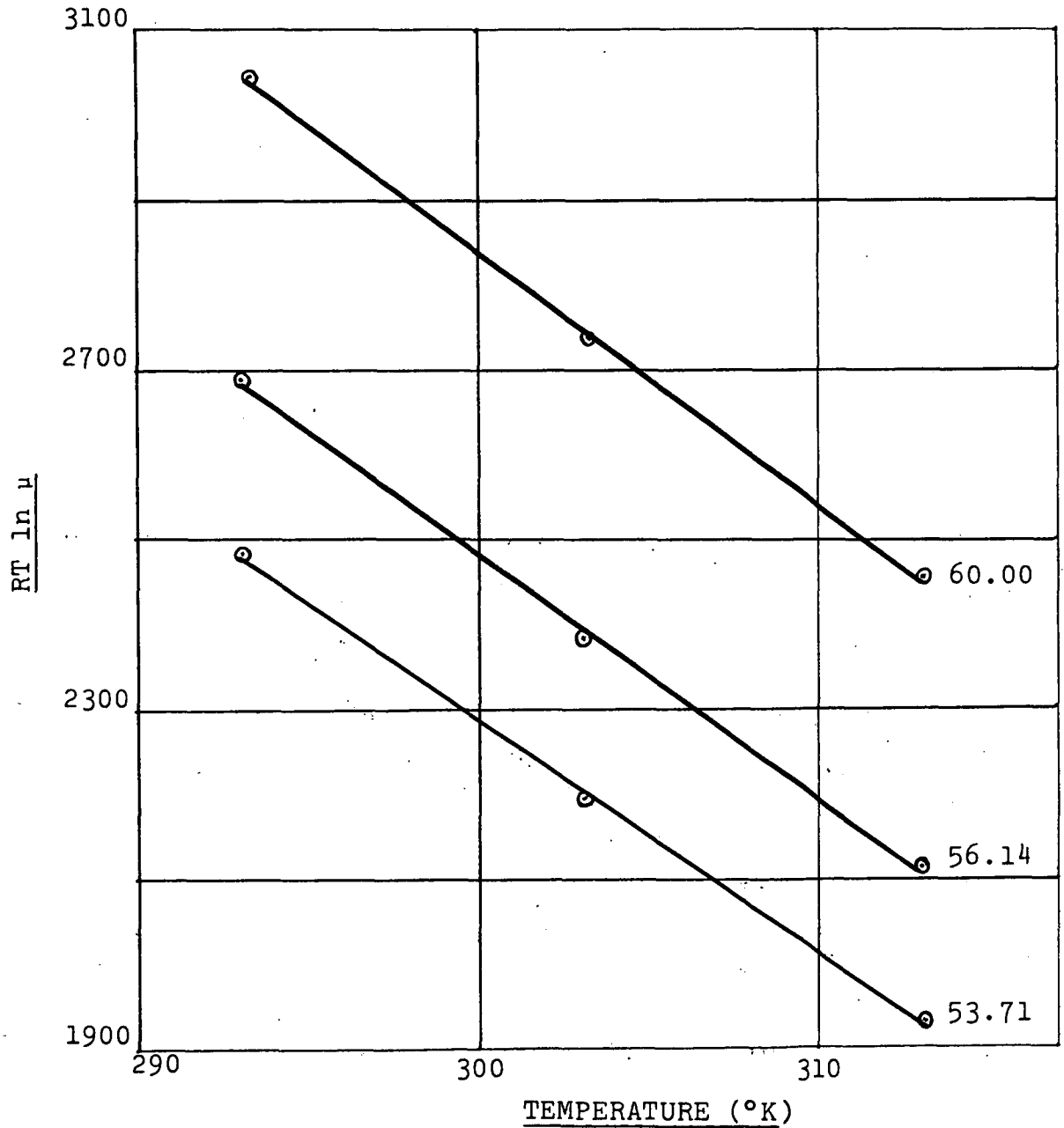


Figure 2-10. $\frac{RT \ln \mu}{V \cdot T}$
0.5 MASS FRACTION OF WATER IN SOLVENT

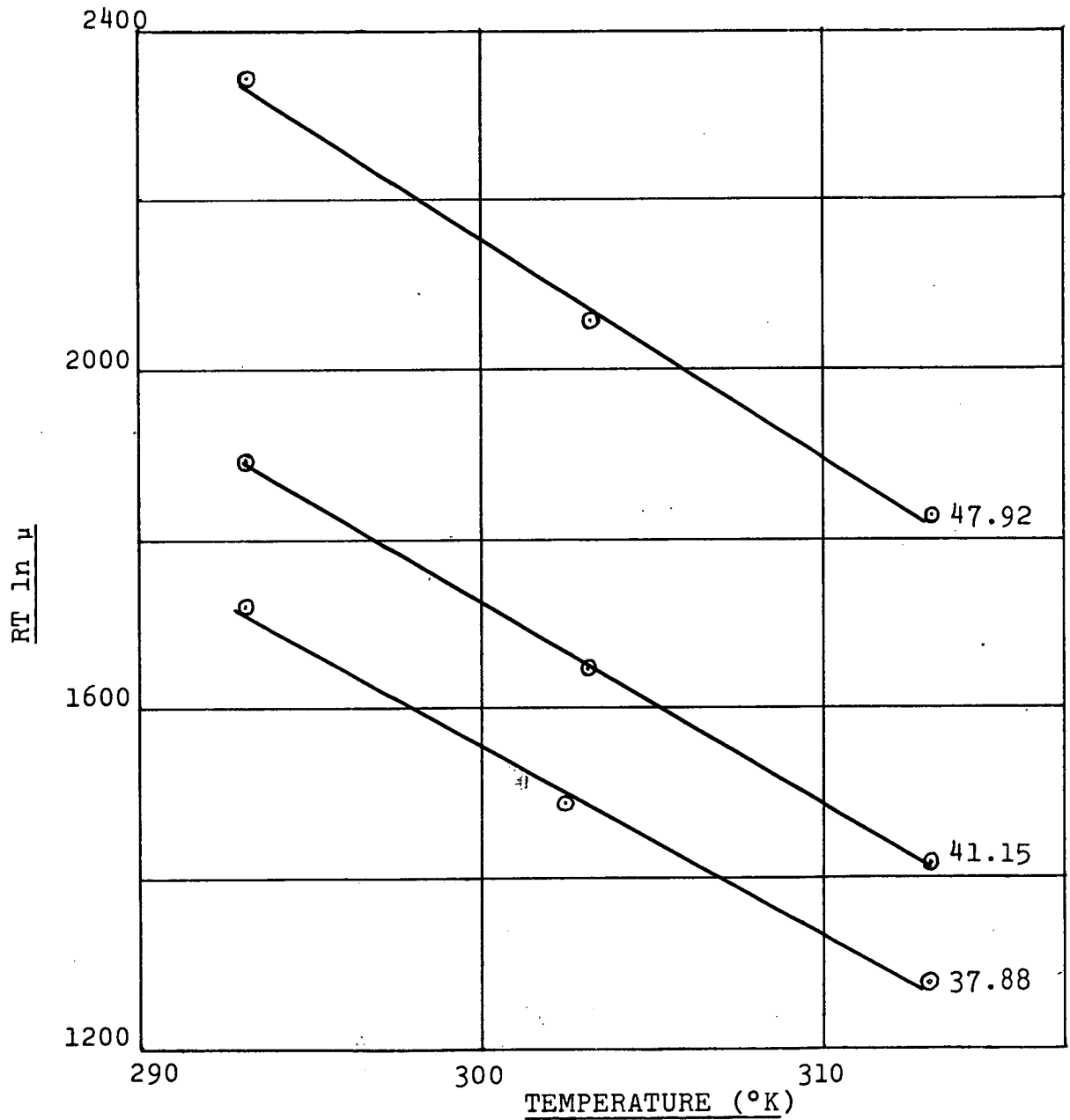


Table 2-4. VISCOSITY ENERGY.

<u>Mass</u> <u>Frac.</u> <u>Water</u>	<u>Satn.</u> <u>Temp.</u> °	<u>S U C R O S E</u>			<u>A</u>	<u>- B</u>	<u>e^Bx10¹⁵</u>	<u>St.D.</u> <u>Rlnμ</u> <u>±%</u>
		<u>%</u>	<u>Molal.</u>	<u>Molefr.</u>				
1.0	20	66.89	5.9019	0.09611	11,971	30.163	79.416	0.70
1.0	30	68.45	6.3382	0.10248	12,447	31.052	32.668	0.52
1.0	40	70.25	6.8985	0.11054	13,514	33.774	2.1477	0.73
0.9	20	63.24	5.5841	0.08794	11,433	28.910	278.22	0.47
0.9	30	65.16	6.0709	0.09488	12,054	30.308	68.748	0.31
0.9	40	67.95	6.8772	0.10620	13,156	32.785	5.7740	0.33
0.8	20	59.68	5.4051	0.08148	11,133	28.586	384.76	
0.8	30	61.24	5.7698	0.08650	11,723	29.885	104.94	
0.8	40	64.03	6.5005	0.09640	12,444	31.124	30.399	
0.7	20	53.71	4.8424	0.06952	10,502	27.373	1293.9	0.27
0.7	30	56.14	5.3419	0.07615	11,087	28.679	350.52	0.31
0.7	40	60.00	6.2602	0.08808	11,694	29.508	153.00	0.17
0.6	20	46.81	4.2850	0.05770	9,540	25.271	10588	
0.6	30	49.75	4.8204	0.06445	10,146	26.689	2564.3	
0.6	40	54.96	5.9414	0.07826	10,905	27.939	734.77	
0.5	20	37.88	3,5691	0.04411	8,247	22.280	210770	0.37
0.5	30	41.15	4.0856	0.05026	8,900	23.915	41088	0.13
0.5	40	47.92	5.3761	0.06509	10,077	26.415	3372.6	0.45

It may be noted that the viscosity energy values calculated in the manner described progressively increase as the sucrose - water molality increases at each water / alcohol ratio, and progressively decreases as the proportion of alcohol in the solvent increases. The over all range covered is from 13.5 to 8.25 k.cal.

The molefraction of sucrose in each solution has been calculated and recorded in Table 2-4, and will be used more specifically in the next chapter when discussions are also concerned with energy values calculated from crystallization studies.

The polynomials used for calculations in this chapter are summarised in Table 2-5, together with the approximate range of application.

Table 2-5. POLYNOMIALS.

(a) 1.0 Mass Fraction of Water in Solvent.

20°: Su = 66-68%:	$\mu = 30,102 - 945.05\text{Su} + 7.45\text{Su}^2$	(2-5)
20°: Su = 68-70%:	$\mu = 64,884.5 - 1,966.55\text{Su} + 14.95\text{Su}^2$	(2-6)
20°: Su = 69-71%:	$\mu = 97,000 - 2,890.85\text{Su} + 21.6\text{Su}^2$	(2-7)
50°: Su = 70-72%:	$\mu = 9,272.9 - 275.05\text{Su} + 2.05\text{Su}^2$	(2-8)
55°: Su = 71-73%:	$\mu = 8,331.4 - 244.3\text{Su} + 1.8\text{Su}^2$	(2-9)
60°: Su = 72-74%:	$\mu = 8,106.0 - 234.2\text{Su} + 1.7\text{Su}^2$	(2-10)
65°: Su = 73-75%:	$\mu = 8,112.2 - 230.85\text{Su} + 1.65\text{Su}^2$	(2-11)
55° - 65° :	$\mu = 2,355.1 - 12.798\text{T} + 0.018\text{T}^2$	(2-12)

(b) 0.8 Mass Fraction of Water in Solvent.

20° - 40°:	$c = 60.33 - 0.1575\text{t} + 0.00625\text{t}^2$	(2-13)
20° - 40°:	$\mu = 28,184.27 - 180.444\text{T} + 0.28944\text{T}^2$	(2-14)

(c) 0.7 Mass Fraction of Water in Solvent.

20° - 40°:	$\mu = 8,535.6 - 55.009\text{T} + 0.08915\text{T}^2$	(2-15)
------------	--	--------

(d) 0.5 Mass Fraction of Water in Solvent.

20° - 40°:	$\mu = 3,137.06 - 20.559\text{T} + 0.03385\text{T}^2$	(2-16)
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(e) Mass Fraction of Water and Minimum Viscosity, Temperature.

(i) 0.5 - 0.8 Mass Fraction of Water:

$$\mu = -146.9 + 433\text{W} - 216.67\text{W}^2 \quad (2-17)$$

$$t = 27.0 - 5.5\text{W} + 25\text{W}^2 \quad (2-18)$$

(ii) 0.7 - 1.0 Mass Fraction of Water:

$$\mu = 46.13 + 163W - 36.667W^2 \quad (2-19)$$

$$t = 363.0 - 905.5W + 625W^2 \quad (2-20)$$

(f) Mass Fraction of Water and Viscosity Energy,
Temperature Coefficient.

(i) 0.5 - 0.9 Mass Fraction of Water: 20°:

$$A = - 3,183 + 31,135W - 16,550W^2 \quad (2-21)$$

$$B = 6.010 - 78.805W + 44.45W^2 \quad (2-22)$$

(ii) 0.5 - 0.9 Mass Fraction of Water: 30°:

$$A = - 1,905 + 29,235W - 15,250W^2 \quad (2-23)$$

$$B = 1.7106 - 70.845W + 39.1875W^2 \quad (2-24)$$

(iii) 0.5 - 0.9 Mass Fraction of Water: 40°:

$$A = 5,356.4 + 10,410W - 1,937.5W^2 \quad (2-25)$$

$$B = - 19.4875 - 12.705W - 2.3W^2 \quad (2-26)$$

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CHAPTER 3. CRYSTALLIZATION RATES AND ENERGY IN
THE SUCROSE - ETHANOL - WATER SYSTEM

1. EXPERIMENTAL METHOD.

The rate of crystal growth was determined by single crystal weight changes. The procedure here adopted was a simplification of that of Smythe¹ (See Chapter 1).

The Apparatus (see Figure 3-1) consisted of the following:-

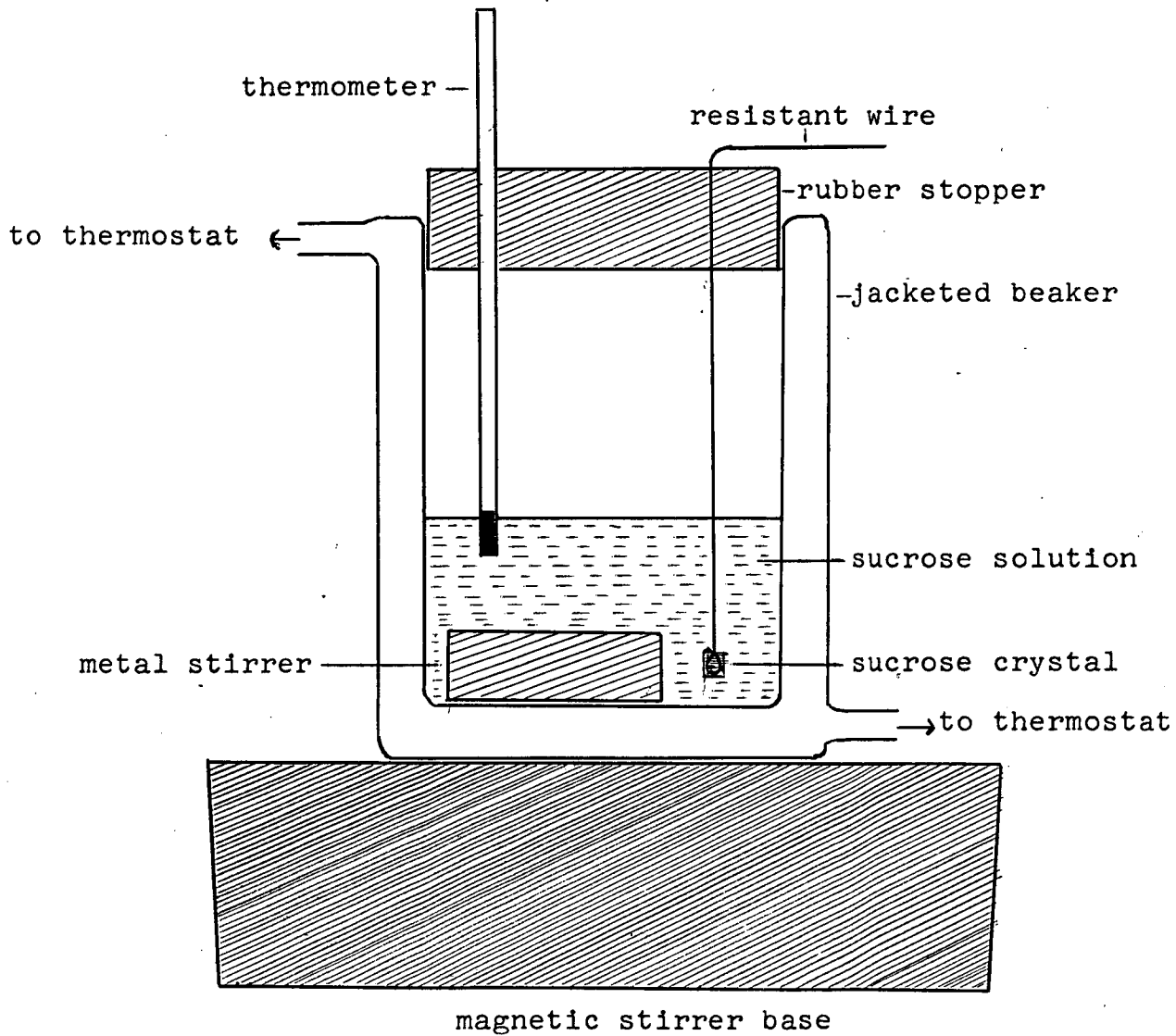
- (1) a jacketed beaker (capacity about 125 c.c.) with connections to circulating water from a Wobser Universal Precision Thermostat;
- (2) a large rubber stopper with holes for a thermometer (3) and wire (4);
- (3) a short-length thermometer;
- (4) a resistance wire used as crystal tongs; and
- (5) a stirrer, electric or magnetic.

Large crystals were used of weight 0.25 g. to 0.7 g. The crystal was suspended with a fine gauge resistance wire (0.213 mm thick) which in turn was joined to thick resistance wire (0.914 mm thick) to hold the suspended crystal in position against the force of the agitated solution. Before each weighing the crystal was released from the wire and dried with soft tissue paper.

45-50 g. solutions were prepared hot and then cooled to the temperature of the Thermostat. The rate of crystallization was determined at three different temperatures. The solutions were the same as in the viscosity experiments.

- (a) The solution saturated at 40° cooled to 30°, 25° and 20°.
- (b) The solution saturated at 30° cooled to 25°, 20° and 15°.
- (c) The solution saturated at 20° cooled to 16°, 13° and 10°.

Figure 3-1. CRYSTAL GROWTH APPARATUS



After various experiments a number of facts became clear for the best work, viz:-

(1) A new solution must be prepared every time as the same solution could not be used at the three temperatures required.

(2) However, the same crystal was used with the three identical solutions at the three temperatures.

(3) Initially the first period of crystal growth was 15 minutes, followed by a number (usually three) of 30 minute periods.

Later the whole series of experiments was repeated with greater precision. A micro balance was used for the crystal weighing, a magnetic stirrer replaced the electric stirrer, the crystal was washed with ethanol before drying, and three 15 minute periods were normally allowed for growth. It is these latter results which are recorded in this chapter. *

2. CALCULATION OF THE CRYSTALLIZATION VELOCITY AND CONSTANT.

The velocity of crystallization according to the formula of Kucharenko² is

$$k = 10^4 \times \Delta p / \sigma \theta \quad \text{mg/m}^2/\text{min.} \quad (3-1)$$

Kucharenko calculated the surface from the formula,

$$\sigma^3 = C_p^2 \quad (1-1)$$

where C averages 69.93.

Actually Kucharenko used crystals of a more cubic shape for his measurements than the crystals which have been used in the current experiments. Kelly^{2a} did a number of measurements some years ago with these particular crystals, and by means of a microscope micrometer measured the dimensions of the various sides and calculated the area by simple geometry. He expressed the result in terms of "sphericity" which is defined as the ratio of the surface area of a sphere of the same volume as the

* The magnetic stirrer speed was 840 r.p.m. or less depending on the viscosity of the solution.

crystal to the actual surface area measured. The value obtained was 0.74. This is equivalent to a value of 110.68 instead of 69.93 or 4.80 instead of 4.12 for the cube root.

The velocity of crystallization therefore becomes, putting both p and Δp in the same units (mg.),

$$k = 10^6 \times \Delta p / 4.80 \times p^{2/3} \times \theta \quad \text{mg/m}^2/\text{min.} \quad (3-2)$$

Van Hook³ has shown that the logarithm of concentration versus time plot, with its middle linear portion, suggests a unimolecular reaction. Smythe¹ similarly maintains that the slopes of the linear portions of the curves, velocity rate versus $(c_s - c)$ at various temperatures, are equivalent to the velocity constant of a first order reaction.

Van Hook uses V for the crystallization velocity and k for the crystallization constant, while Smythe following Kucharenko denotes the crystallization velocity by n , but the general practice has been to call k the crystallization velocity, and this is adhered to in the current studies. The suggested unimolecular reaction may then be put in the following form, crystallization velocity,

$$k = n (c - c_s) \quad (3-3)$$

The crystallization constant (n) was therefore calculated from formula (3-3). It was necessary to find solubility equations for the various sets of solutions so that solubilities at 10°, 13°, 15°, 16° and 25° could be calculated. (See Table 3-6).

Table 3-1 records the Crystallization Velocities and Constants for the various solutions.

Table 3-1. CRYSTALLIZATION VELOCITIES AND CONSTANTS.

<u>Mass</u> <u>Fractn.</u> <u>Water</u>	<u>Satn.</u> <u>Temp.</u> <u>°</u>	<u>SOLUTION COMPOSITION</u> <u>(weight percent)</u>			<u>Temp.</u> <u>°</u>	<u>CRYSTALLIZATION</u>	
		<u>Sucrose</u>	<u>Ethanol</u>	<u>Water</u>		<u>Velocity</u>	<u>Constant</u>
1.0	20	66.89	0	33.11	10	484.9	41.91
1.0	20	66.89	0	33.11	13	427.5	52.01
1.0	20	66.89	0	33.11	16	338.3	67.66
1.0	30	68.45	0	31.55	15	870.9	41.27
1.0	30	68.45	0	31.55	20	784.7	52.51
1.0	30	68.45	0	31.55	25	716.1	90.20
1.0	40	70.25	0	29.75	20	1188	34.04
1.0	40	70.25	0	29.75	25	1395	51.45
1.0	40	70.25	0	29.75	30	1425	74.34
0.9	20	63.24	3.676	33.084	10	390.5	52.05
0.9	20	63.24	3.676	33.084	13	403.9	67.55
0.9	20	63.24	3.676	33.084	16	419.6	109.5
0.9	30	65.16	3.484	31.356	15	684.5	34.91
0.9	30	65.16	3.484	31.356	20	616.6	41.13
0.9	30	65.16	3.484	31.356	25	609.0	71.39
0.9	40	67.95	3.205	28.845	20	1243	27.68
0.9	40	67.95	3.205	28.845	25	1561	40.58
0.9	40	67.95	3.205	28.845	30	1440	48.12
0.7	20	53.71	13.887	32.403	10	265.5	58.10
0.7	20	53.71	13.887	32.403	13	273.2	70.06
0.7	20	53.71	13.887	32.403	16	275.3	104.69
0.7	30	56.14	13.158	30.702	15	530.0	35.13
0.7	30	56.14	13.158	30.702	20	435.2	36.36
0.7	30	56.14	13.158	30.702	25	354.3	50.61
0.7	40	60.00	12.000	28.000	20	826.0	24.32
0.7	40	60.00	12.000	28.000	25	967.9	33.38
0.7	40	60.00	12.000	28.000	30	1079	49.02

Table 3-1. CRYSTALLIZATION VELOCITIES AND CONSTANTS (cont'd).

<u>Mass</u> <u>Fractn.</u> <u>Water</u>	<u>Satn.</u> <u>Temp.</u> <u>°</u>	<u>SOLUTION COMPOSITION</u> <u>(weight percent)</u>			<u>Temp.</u> <u>°</u>	<u>CRYSTALLIZATION</u>	
		<u>Sucrose</u>	<u>Ethanol</u>	<u>Water</u>		<u>Velocity</u>	<u>Constant</u>
0.5	20	37.88	31.060	31.060	10	208.3	32.45
0.5	20	37.88	31.060	31.060	13	179.8	38.07
0.5	20	37.88	31.060	31.060	16	206.0	72.60
0.5	30	41.15	29.425	29.425	15	510.7	41.08
0.5	30	41.15	29.425	29.425	20	392.7	43.90
0.5	30	41.15	29.425	29.425	25	338.6	70.13
0.5	40	47.92	26.040	26.040	20	1475	47.52
0.5	40	47.92	26.040	26.040	25	1992	73.99
0.5	40	47.92	26.040	26.040	30	1889	85.50

3. COMMENTS ON THE CRYSTALLIZATION VELOCITY.

The Table of results looks very simple, but it conveys no conception of the necessary study of the experimental data in order to secure results which in the following Table (3-2) of Energy Values form a coherent whole. It is obvious that the method here adopted to calculate the crystallization energy of the various solutions has serious limitations.

For example, what exactly is the Crystallization Velocity, It varies very considerably and depends on the actual time taken and when in the course of crystal growth.

Smythe¹ continued a run for 1-3 hours, although he was convinced that for most purposes the required precision could be secured by the increase in weight during the first hour.

However, Whittier and Gould⁴, using the refractometric method described in chapter 1, discarded the values for the early and late portions, since they showed extreme variations. This has been kept in mind in the present work.

It might be argued that the way to estimate the crystallization rate in these studies in this chapter is to take the average over the entire 45 minute period. This is certainly carried out where it is possible, but it is not always satisfactory.

In the present chapter experiments are recorded which have been carried out at various temperatures. There is a consistency about this experimental work at one temperature, but to relate crystallization velocities at different temperatures, and from the relation to calculate the crystallization energy, has not been without difficulties.

Crystal growth appears to be slower in the first 15 minutes at the lower temperatures, 10° - 16° . However, at temperatures 20° - 30° , the growth is usually much greater in the first period, and this increase in weight may therefore have to be treated with caution. In the latter case, an average of the second and third 15 minute readings would give a much better figure for the crystallization velocity than an average of the three readings. It is just here that there is the great benefit of taking three separate readings (in spite of the time involved with the micro balance which requires 15-20 minutes before there is a stable reading of the crystal weight). The refined technique means that the crystallization rate is of an almost instantaneous value, there being no significant change in degree of saturation of the solution.

This means that there is no set way of estimating the crystallization velocity in the various solutions under consideration. However, in the following chapter, working at the temperatures 20° , 30° and 40° , and where there is no relation to be determined between crystallization velocities at different temperatures, the principle has been adopted of rejecting the first (high) reading, and majoring on the second (medium) reading. The third reading is often low and is

rejected. But if the second and third readings are fairly close, their average gives a good reading for the calculation of the crystallization velocity.

Instead of the various possibilities for the crystallization velocity being listed, what appeared to be the best figure under the circumstances was chosen. The figures secured for the crystallization rates are therefore relative, and are not truly comparable with the more absolute results of the following chapter (in the case of aqueous sucrose solutions).

It is concluded that as far as these studies are concerned, there is an approximation about the values of the crystallization velocity in the system under consideration.

4. CRYSTALLIZATION ENERGY.

Following Van Hook³, crystallization constants are used to calculate activation energies of crystallization. In these current studies the Arrhenius equation is utilised in the form,

$$RT \ln n = A + BT \quad (3-4)$$

The systems being studied have been plotted with these coordinates in Figures 3-2, 3-3, 3-4 and 3-5. In each instance B (the slope), the temperature coefficient, and A (the anti-log of the intercept) have been calculated.

Table 3-2 summarises the results secured. The values for 0.8 and 0.6 mass fractions of water have been interpolated from polynomials formed from the 0.9, 0.7 and 0.5 values.

This method of calculating the crystallization energy depends on the validity of the linear relationship,

$$n = k / (c - c_s) \quad (3-3)$$

It will be demonstrated in the next chapter that this breaks down near saturation. The high values of the crystallization constant with 20° saturation solutions of the 0.9 and 0.7 mass fractions of water at 16° are doubtless due to
(cont'd p 3-13)

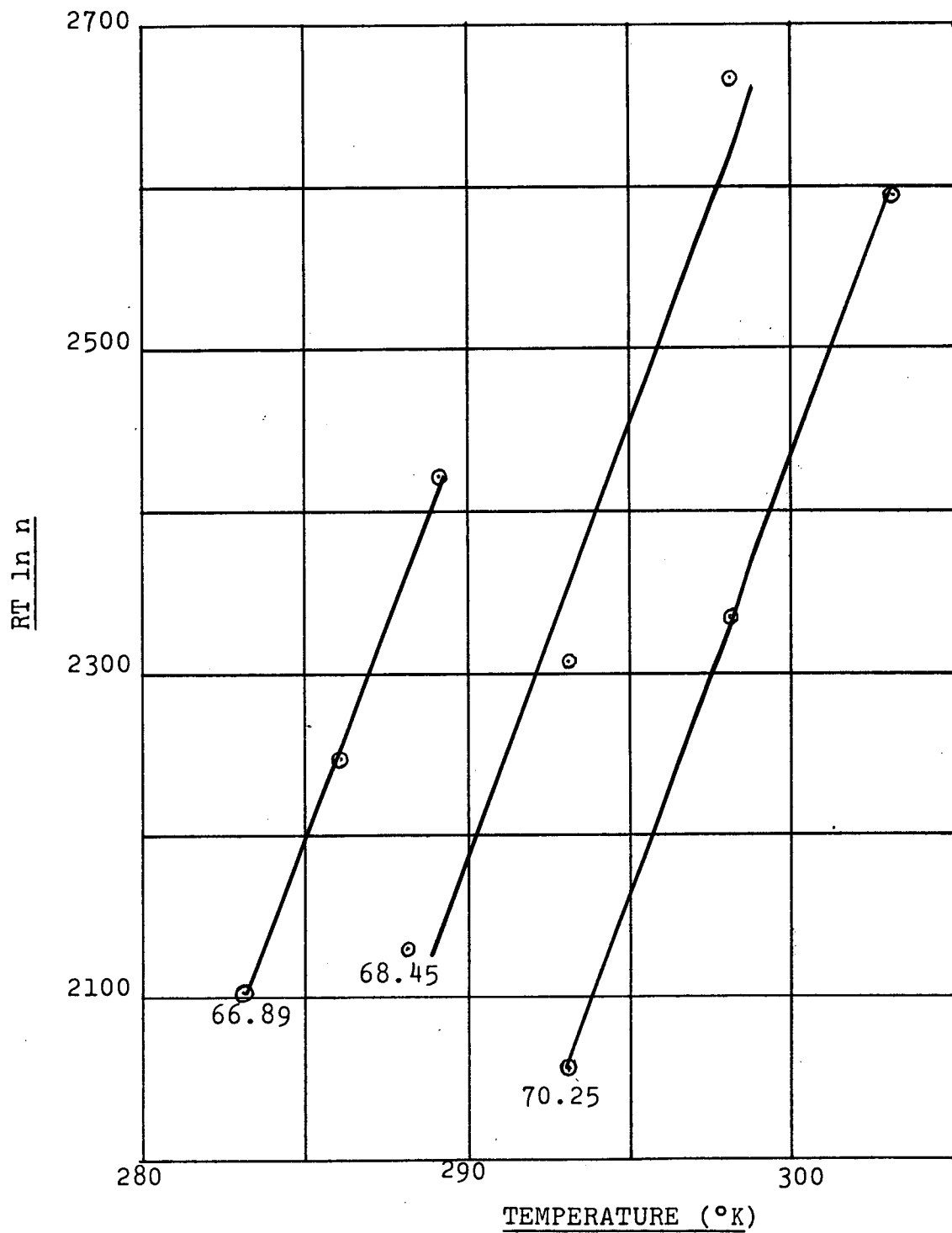
Figure 3-2. $RT \ln n$ V. T.1.0 MASS FRACTION OF WATER IN SOLVENT

Figure 3-3. $RT \ln n$ V. T .

0.9 MASS FRACTION OF WATER IN SOLVENT

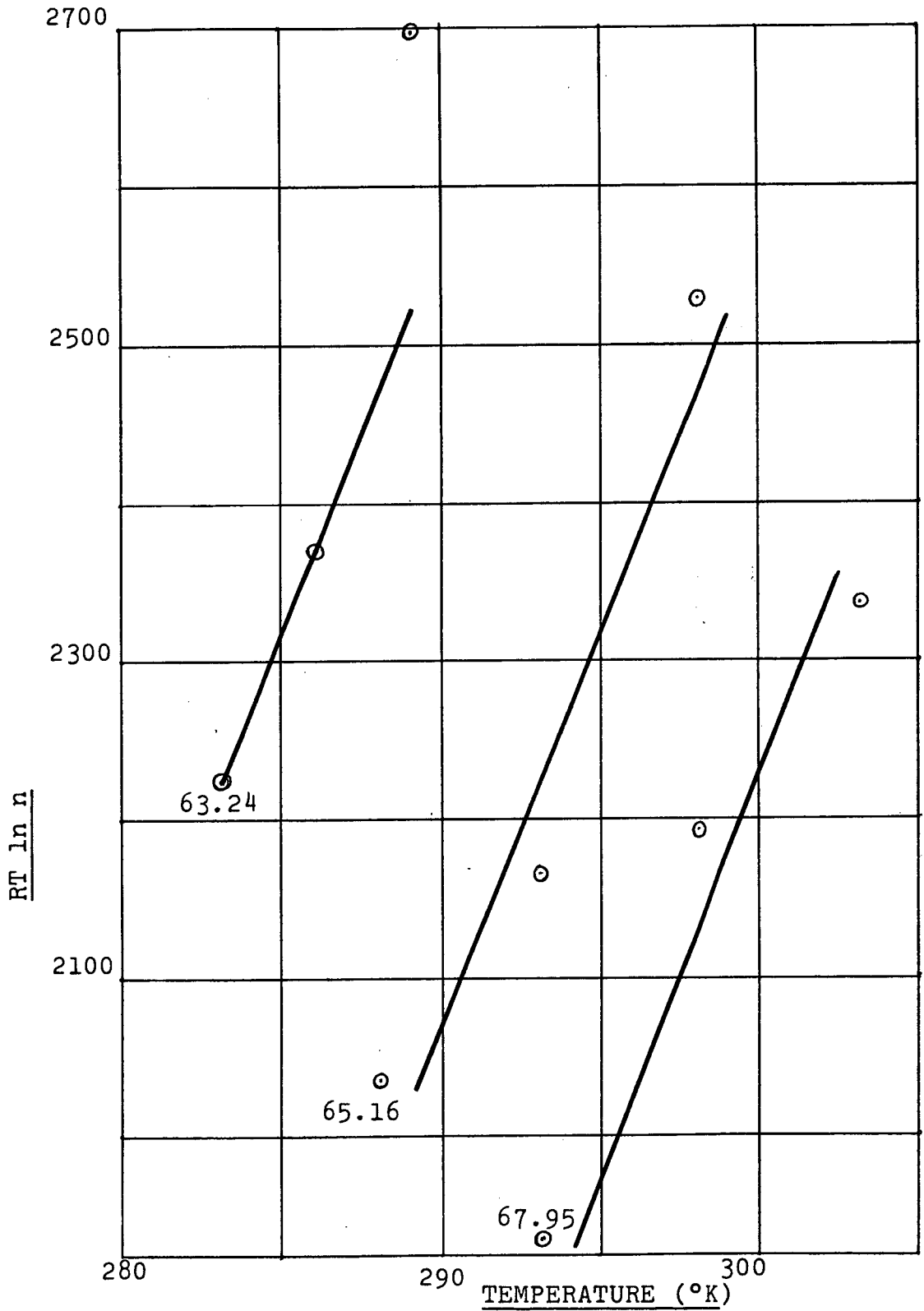


Figure 3-4. $RT \ln n$ V. T .

0.7 MASS FRACTION OF WATER IN SOLVENT

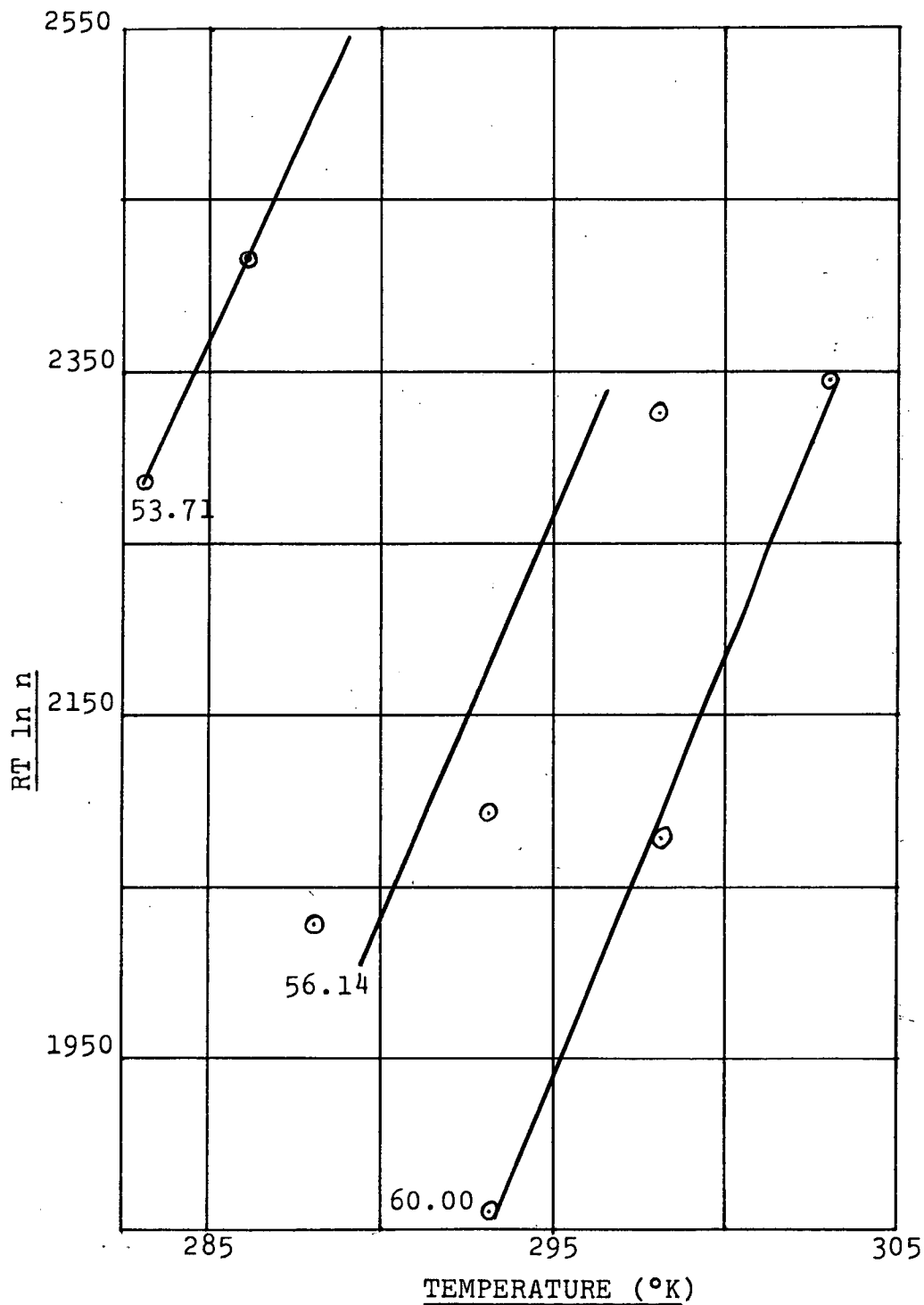


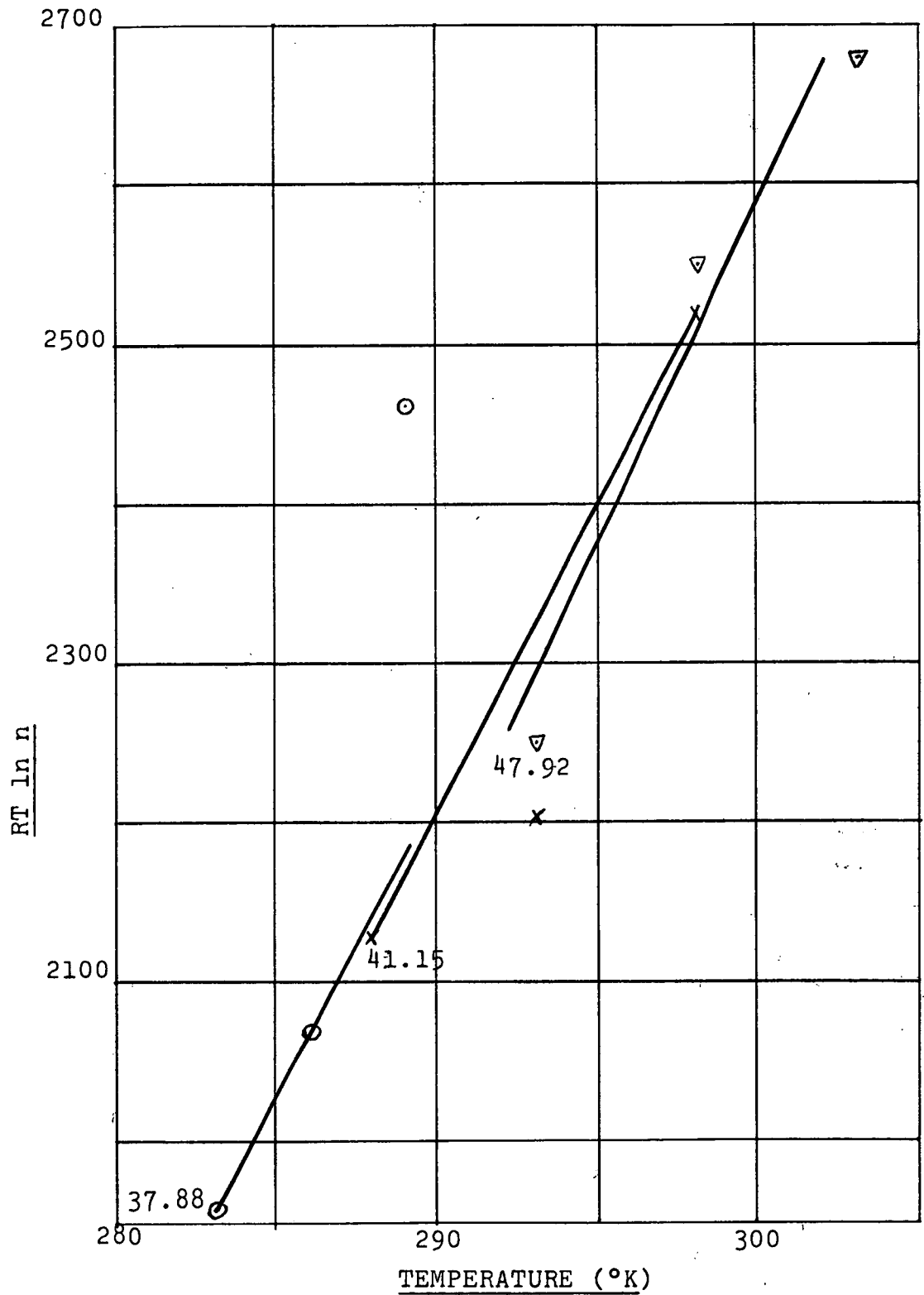
Figure 3-5. $RT \ln n$ V. T .0.5 MASS FRACTION OF WATER

Table 3-2. CRYSTALLIZATION ENERGY.

Standard deviation is expressed as a percentage of the calculated value.

<u>Mass</u> <u>Fractn.</u> <u>Water</u>	<u>Satn.</u> <u>Temp.</u> °	<u>S U C R O S E</u>			- <u>A</u>	<u>B</u>	± <u>St. D.</u> <u>R ln n</u>
		<u>%</u>	<u>Molal.</u>	<u>Molefr.</u>			
1.0	20	66.89	5.9019	0.09611	12,998	53.300	0.30
1.0	30	68.45	6.3382	0.10248	13,410	53.770	1.92
1.0	40	70.25	6.8985	0.11054	13,801	54.100	0.39
0.9	20	63.24	5.5841	0.08794	11,613	48.867	4.17
0.9	30	65.16	6.0709	0.09488	12,276	49.460	2.63
0.9	40	67.95	6.8772	0.10620	13,346	51.920	2.51
0.8	20	59.68	5.4051	0.08148	10,822	46.430	
0.8	30	61.24	5.7698	0.08650	12,019	48.433	
0.8	40	64.03	6.5005	0.09640	13,011	50.528	
0.7	20	53.71	4.8424	0.06952	10,050	43.567	2.83
0.7	30	56.14	5.3419	0.07615	11,409	46.360	4.52
0.7	40	60.00	6.2602	0.08808	12,398	48.590	0.55
0.6	20	46.81	4.2850	0.05770	9,298	40.480	
0.6	30	49.75	4.8204	0.06445	10,447	43.243	
0.6	40	54.96	5.9414	0.07826	11,507	46.108	
0.5	20	37.88	3.5691	0.04411	8,566	37.167	7.42
0.5	30	41.15	4.0856	0.05026	9,133	39.080	3.00
0.5	40	47.92	5.3761	0.06509	10,338	43.080	1.73

4. CRYSTALLIZATION ENERGY (cont'd).

the low supersaturation, $S = 1.023$, in each case. These values have been ignored in the calculation of the crystallization energy.

It is notable that the highest standard deviation (7.42% of

calculated value) occurs with 0.5 mass fraction of water at 20°. The high crystallization constant of this 20° saturated solution at 16° would appear to be related to the low supersaturation, $S = 1.049$. This value has been rejected in the calculation of the crystallization energy.

The three plots (Figure 3-5) for 0.5 mass fraction of water are rather complicated by their proximity to each other, and it has also been necessary to ignore the 20° value for the 30° saturated solution. Further experiments with the 40° saturated solution gave no better results in an endeavour to separate the plots.

The energy values range from about 13.8 to 8.55 k.cal. A study of these crystallization energy values and the viscosity energy values which range from 13.5 to 8.25 k.cal. (Table 2-4) indicates substantial similarity between them. Even allowing for the fact that there is an approximation about the former values, it would appear that the system is viscosity controlled.

5. THEORETICAL CRYSTALLIZATION ENERGY CALCULATIONS.

$$RT \ln S_u = A + BT \quad (3-5)$$

where S_u is defined as sucrose viewed as a molefraction, as a mass fraction, and as molality with respect to water as solvent, is plotted in Figures 3-6, 3-7 and 3-8. Since the plots are not linear, it suggests the addition of a further power of T , i.e.

$$RT \ln S_u = A + BT + CT^2 \quad (3-6)$$

The energy values secured are set out in Tables 3-3, 3-4 and 3-5, together with the calculated minimum values of the plots.

Figure 3-6. $RT \ln Su$ V. T .
(where Su is Molefraction of Sucrose)

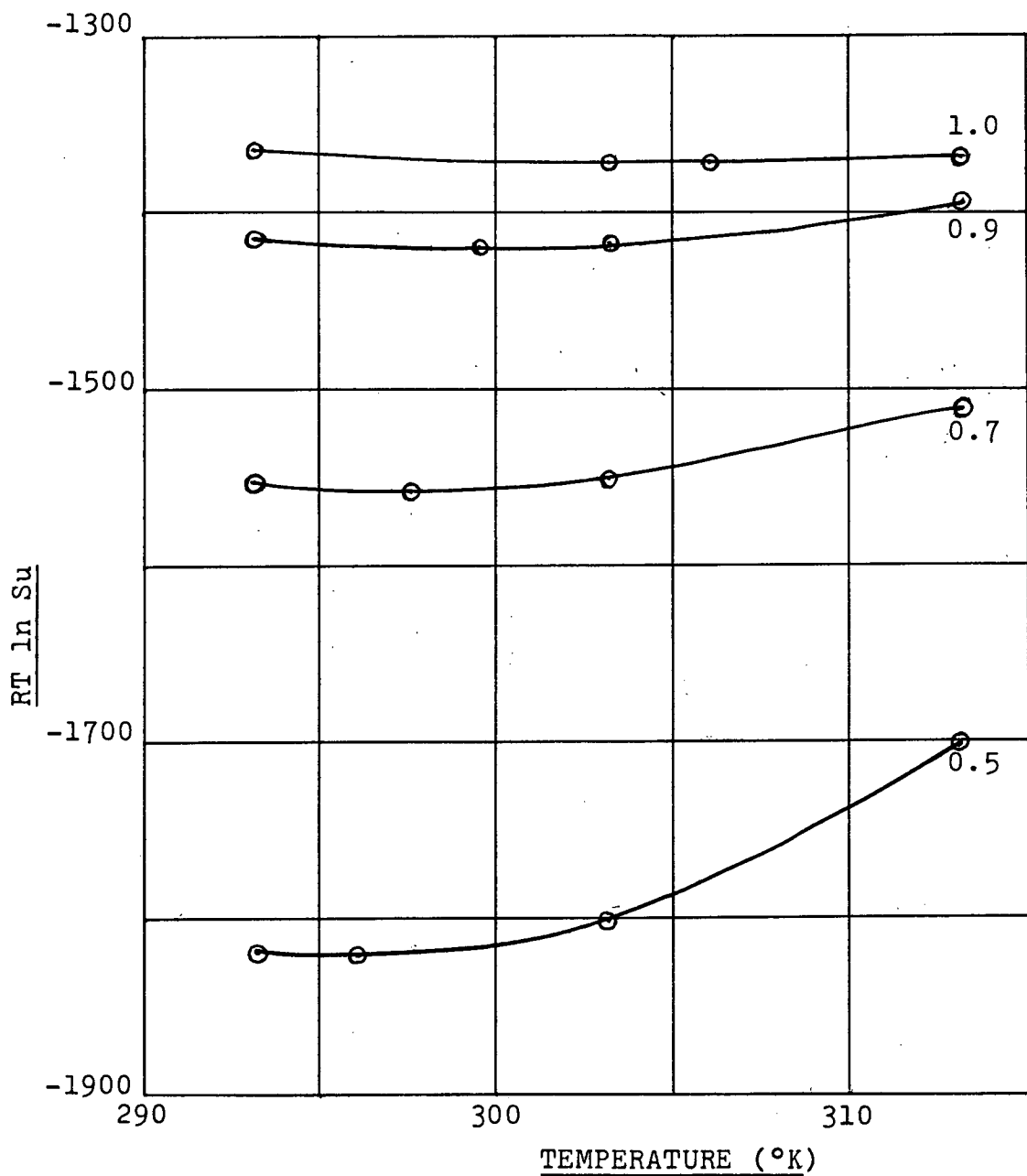


Figure 3-7. $RT \ln S_u$ V. T .
(where S_u is Mass Fraction of Sucrose)

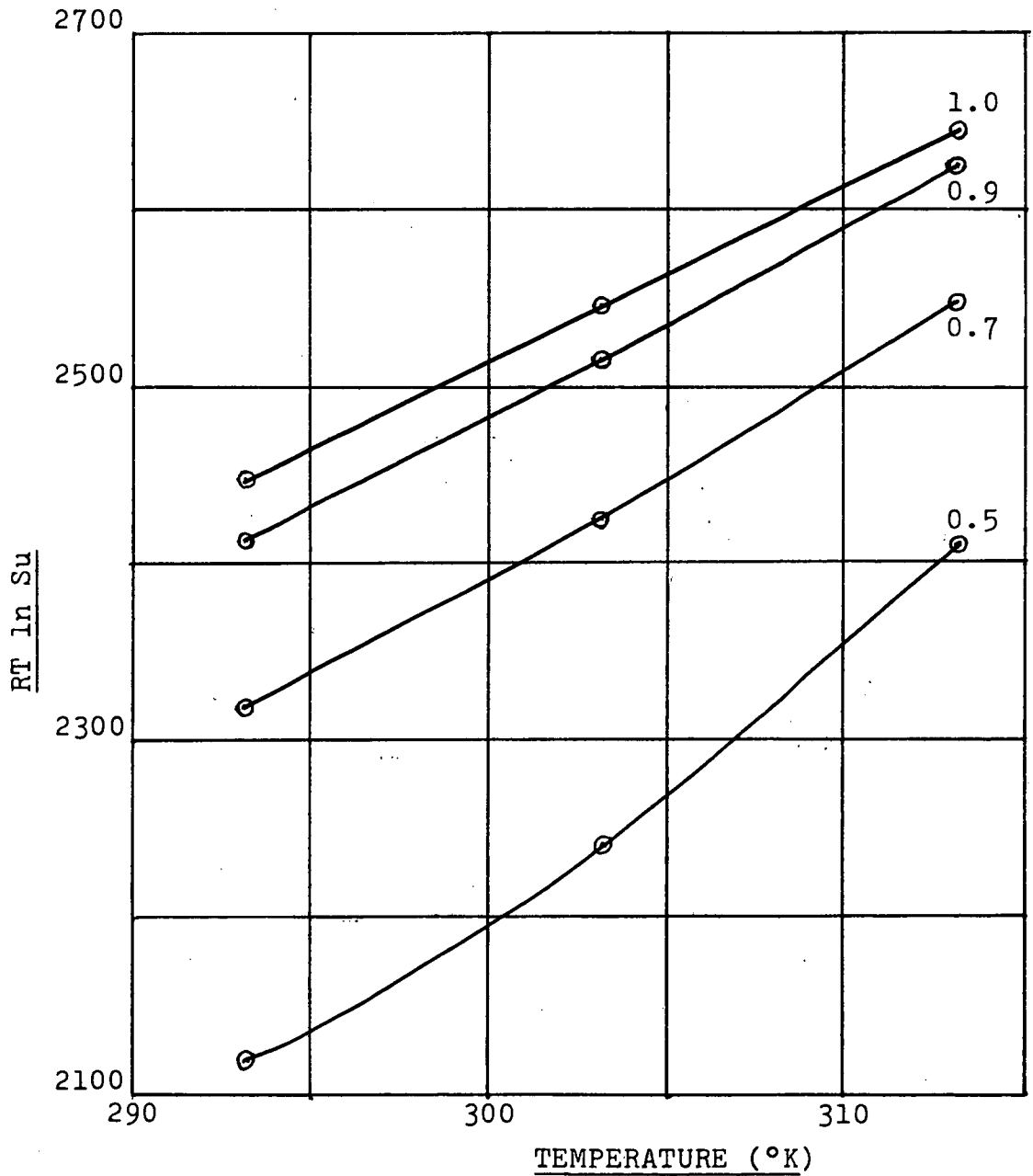


Figure 3-8. $RT \ln Su$ V. T .
(where Su is Molality with respect
to water)

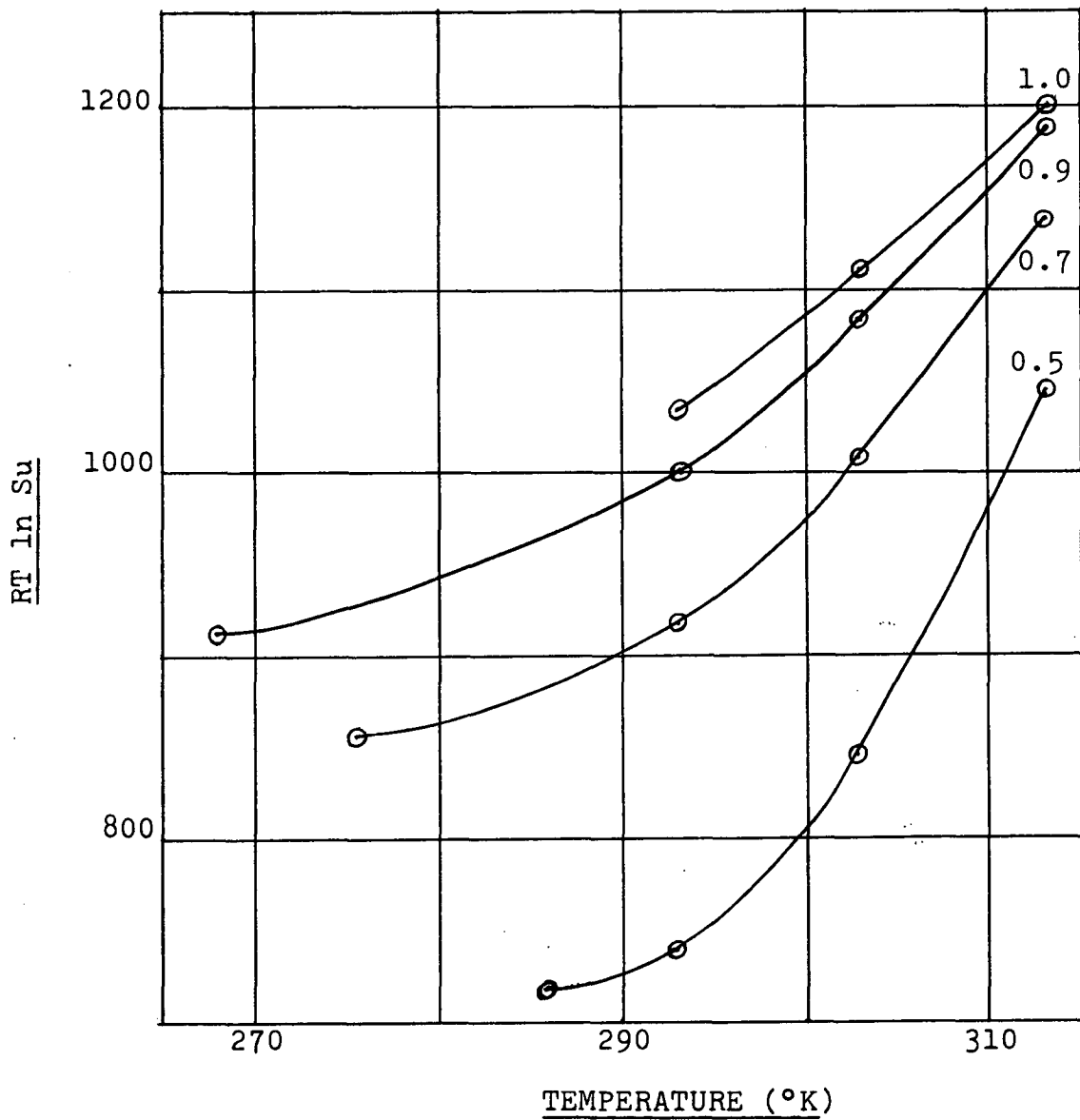


Table 3-3. CRYSTALLIZATION ENERGY VALUES Related to Sucrose Concentration as Molefraction of Solution.

<u>Mass Fraction of Water</u>	<u>A</u>	<u>- B</u>	<u>C</u>	<u>Minimum</u>	
				<u>-RTlnSu</u>	<u>T</u>
1.0	3,204	29.890	0.04881	1372.5	306.2
0.9	9,892	75.649	0.12647	1420	299.1
0.7	14,658	108.987	0.18314	1557	297.6
0.5	34,425	244.871	0.41356	1820	296.1

Table 3-4. CRYSTALLIZATION ENERGY VALUES Related to Sucrose Concentration as Mass Fraction of Solution.

<u>Mass Fr. of Water</u>	<u>A</u>	<u>- B</u>	<u>e^B</u>	<u>C</u>	<u>Minimum</u>	
					<u>RTlnSu</u>	<u>T</u>
1.0	730	-2.114	8.2774	0.01279	1777.7	-82.6
0.9	3,216	15.095	2.7810×10^{-7}	0.04218	1865.6	179.0
0.7	6,000	34.933	9.1855×10^{-16}	0.07635	2004.0	228.8
0.5	18,757	123.49		0.22762	2008.0	271.3

It was obvious that the first three plots in Figure 3-7 were approximately linear. Thus CT^2 could be ignored, and e^B would be the frequency factor, and this has been calculated. The unreal nature of the minimum temperatures in the first three plots in Figure 3-7 is notable.

Table 3-5. CRYSTALLIZATION ENERGY VALUES Related to Sucrose Concentration as Molality with Respect to Water.

<u>Mass Fr. Water</u>	<u>A</u>	<u>- B</u>	<u>C</u>	<u>Min. RTlnSu</u>	<u>Min. T</u>
1.0	3,635	25.022	0.05509	793.9	227.1
0.9	11,041	75.557	0.14093	913.8	268.1
0.7	16,203	111.344	0.20197	857.0	275.7
0.5	37,419	256.503	0.44819	719.0	286.2

The energy values in Table 3-5 are somewhat similar to those in Table 3-3.

The polynomials used in calculations in this chapter are summarised in Table 3-6 having been applied to tabulated values.

Table 3-6. POLYNOMIALS.

(a) Solubility Equations. 10° - 50°:

$$1.0 \text{ Mass Fr. of Water: } c = 64.49 + 0.096t + 0.0012t^2 \quad (3-7)$$

$$0.9 \text{ Mass Fr. of Water: } c = 62.01 - 0.0255t + 0.00435t^2 \quad (3-8)$$

$$0.7 \text{ Mass Fr. of Water: } c = 53.14 - 0.1145t + 0.00715t^2 \quad (3-9)$$

$$0.5 \text{ Mass Fr. of Water: } c = 33.41 + 0.1545t + 0.00345t^2 \quad (3-10)$$

This last equation (3-10) is only over the range 10° - 30°. The polynomial formed from the tabular values was,

$$c = 41.84 - 0.548t + 0.0175t^2 \quad (3-11)$$

This polynomial appeared unsatisfactory as it gave a minimum solubility at 15.7°, and it was therefore considered best to omit the 40° solubility figure, and add a 10° solubility value from crystal growth studies. Five experiments were carried out at 10° until an approximate value of the solubility was found at 35.30%.

(b) Mass Fraction of Water and Crystallization Energy,

Temperature Coefficient. 0.5 - 0.9 Mass Fraction of Water:

$$(i) \ 20^\circ: \ A = 5,201.6 + 6,235W + 987.5W^2 \quad (3-12)$$

$$B = 17.2295 + 45.5W - 11.25W^2 \quad (3-13)$$

$$(ii) \ 30^\circ: \ A = -2,721.4 + 32,515W - 17,612.5W^2 \quad (3-14)$$

$$B = 2,592.5 + 99.1W - 52.25W^2 \quad (3-15)$$

$$(iii) \ 40^\circ: \ A = 323 + 26,980W - 13,900W^2 \quad (3-16)$$

$$B = 19,767.5 + 60.25W - 27.25W^2 \quad (3-17)$$

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2. Kucharenko, J.A., Planter Sugar Mfr, Vol 80, Nos 22,23 (1928).
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3. Van Hook, A., Principles of Sugar Technology II (Ed. Honig), (1959), 149-166.
4. Whittier, E.O., and Gould, S.P., Ind. Eng. Chem (1931), 23, 670.

* 2A. Kelly, F.H.C., I.S.J. 1957, 59, 304.

CHAPTER 4. CRYSTALLIZATION AND SOLUTION STUDIES
IN AQUEOUS SUCROSE SOLUTIONS

The refined technique for determining the crystallization velocity described in chapter 3 was also used in a series of experiments restricted to pure sucrose aqueous solutions. At high supersaturations (over $S = 1.80$) it was found best only to have two readings, and to limit these to 10 minutes each, owing to the rapid occurrence of spontaneous nucleation.

This method was also applied in ascertaining the velocity of solution. At undersaturation less than $S = 0.90$ it was preferred to limit periods of observation to 10 minutes each. In the rate of solution studies, the crystal dissolved in the solution, and the decrease in weight was measured with the micro balance.

It appears best to regard the solution velocity as a negative crystallization velocity while the solution constant like the crystallization constant is positive.

It was decided to limit studies to the temperatures, 20° , 30° and 40° .

1. CRYSTALLIZATION AND SOLUTION VELOCITIES.

It is recorded that there is some rationalization of results since different crystals gave different values for the velocity of crystallization or solution. Therefore the same crystal was used as much as possible in order to obtain consistent figures. Also, in using the same crystal it was necessary to minimize change in weight, preferably to less than 0.1 g.

One of the important matters in studies in this field is competence in the calculation of the two velocities near saturation. In this region change in concentration of the solution cannot be regarded as negligible, and hence there is substantial disparity between readings, with the third often

becoming extremely small. This indicated the advantage in taking three separate readings of 15 minutes each rather than being committed to the average reading over 45 minutes.

It has been usual in these studies to reject the first reading if it is higher than the other readings, and to take the second reading near saturation. However, if the second and third readings are close to each other, a satisfactory figure for the velocity has been secured by combining both readings. It will be obvious that the figure thus gained could significantly differ from that determined from one reading over one hour.

It was found to be much more difficult to determine velocities at 40° since there was a tendency for crystals to break readily. At this temperature crystals lasted for about four experiments before breaking. However, at 20° and 30° the same crystal could be used continually.

When working with the same crystal in both undersaturated and supersaturated solutions, it was apparent that the growth and dissolution of the crystal did not balance out, in spite of the lowest undersaturation being only about $S = 0.850$. This was taken to indicate that the rate of solution is much greater than that of crystallization.

In this chapter the unit for crystallization and solution velocities has been changed from $\text{mg}/\text{m}^2/\text{min}$. used in chapter 3 for the crystallization velocity. Following on Kelly's concept of "sphericity" (p 3-3), a crystal may be regarded as equivalent to a sphere of the same volume, its growth or dissolution being indicated by the increase or decrease of the sphere diameter. From this point of view the crystallization or solution velocity may be defined as follows:-

$$k = (d_2 - d_1) / \theta \quad \text{microns / min.} \quad (4-1)$$

Since the volume of a sphere is $\pi d^3/6$ and the density of sugar is 1.588 g/ml,

$$\begin{aligned} d &= (6 \times 10^9 / 1.588 \times 3.14159)^{1/3} p^{1/3} \text{ microns} \\ &= 1.06345 \times 10^3 p^{1/3} \text{ microns} \end{aligned} \quad (4-2)$$

The values secured for the crystallization and solution velocities using formulae (4-1) and (4-2) are set out in Tables 4-1 and 4-2 respectively, together with the saturation coefficient (c/c_s) calculated to Kelly solubility data. Tables 4-1 and 4-2 are placed after Figures 4-1, 4-2 and 4-3 since they also contain information relevant to the next section of the chapter.

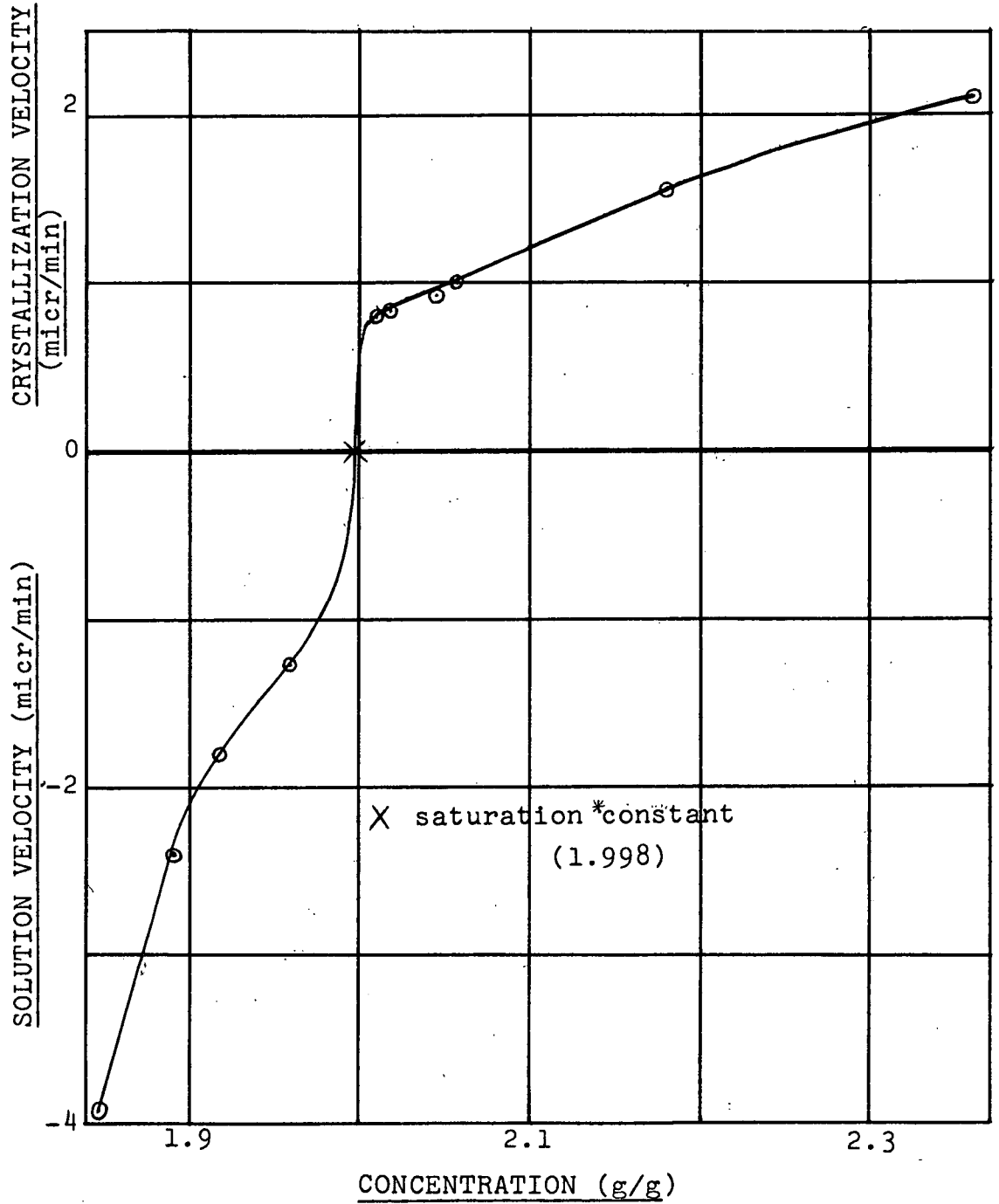
The relationship between both the crystallization and solution velocities and concentration (g sucrose / g water) is illustrated in Figures 4-1, 4-2 and 4-3 for the three temperatures under consideration. For these plots to give useful figures for solubility at the three temperatures, it was thought best to only use the lower values of the crystallization velocities and higher values of the solution velocities.

The solubility values obtained are as follows:-
1.998 g/g at 20°, 2.130 g/g at 30°, and 2.300 g/g at 40°.

The current studies will now prefer the use of these new interpolated solubility figures (hereafter referred to as Tuck solubility) as well as the original Kelly values. The saturation coefficients calculated to Tuck solubility are also recorded in Tables 4-1 and 4-2.

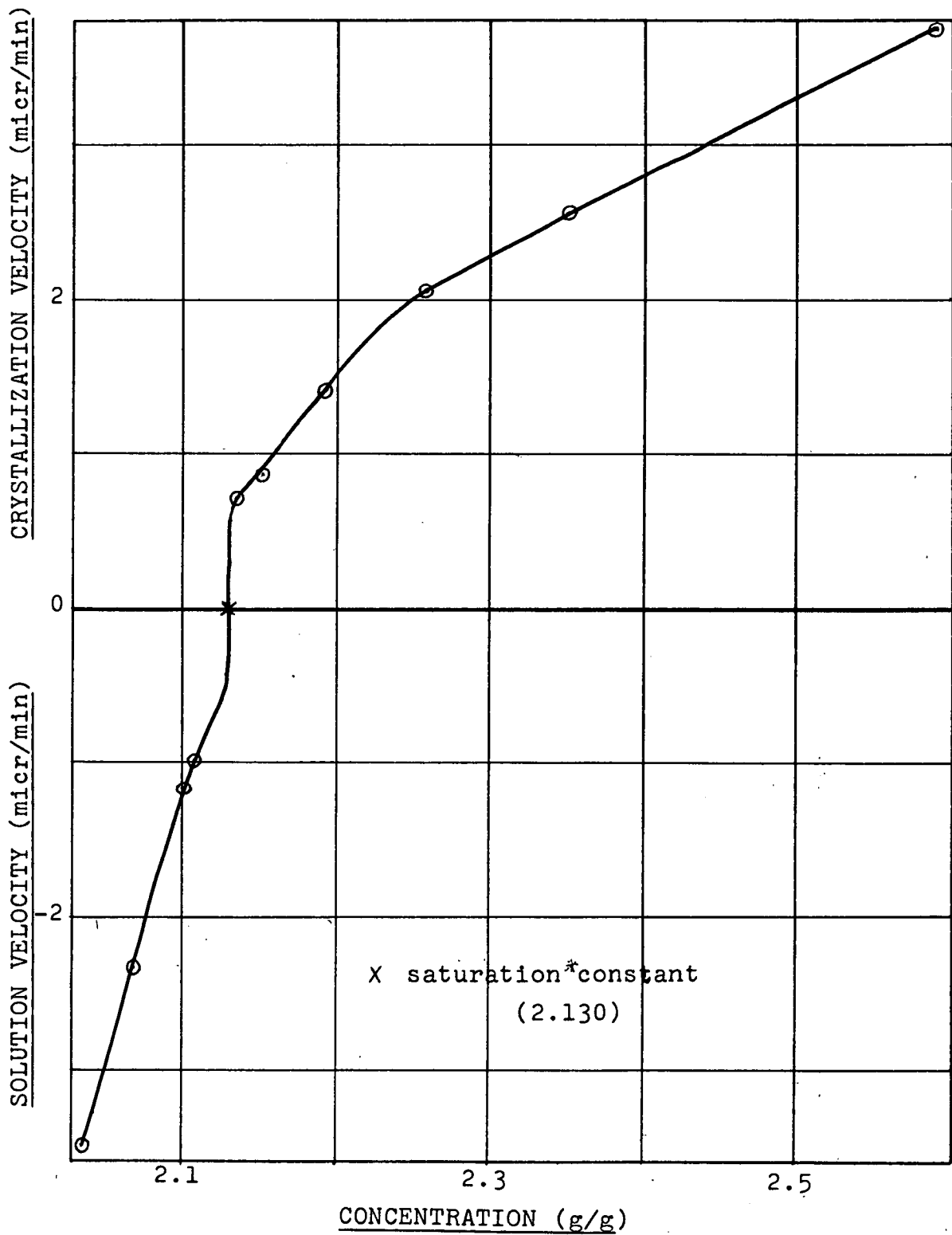
The graphs (Figures 4-1, 4-2 and 4-3) show very clearly the difference in magnitude between the crystallization and solution velocities when displacements from saturation are equal, especially at 20°.

Figure 4-1. CRYSTALLIZATION AND SOLUTION VELOCITIES
V. CONCENTRATION AT 20°



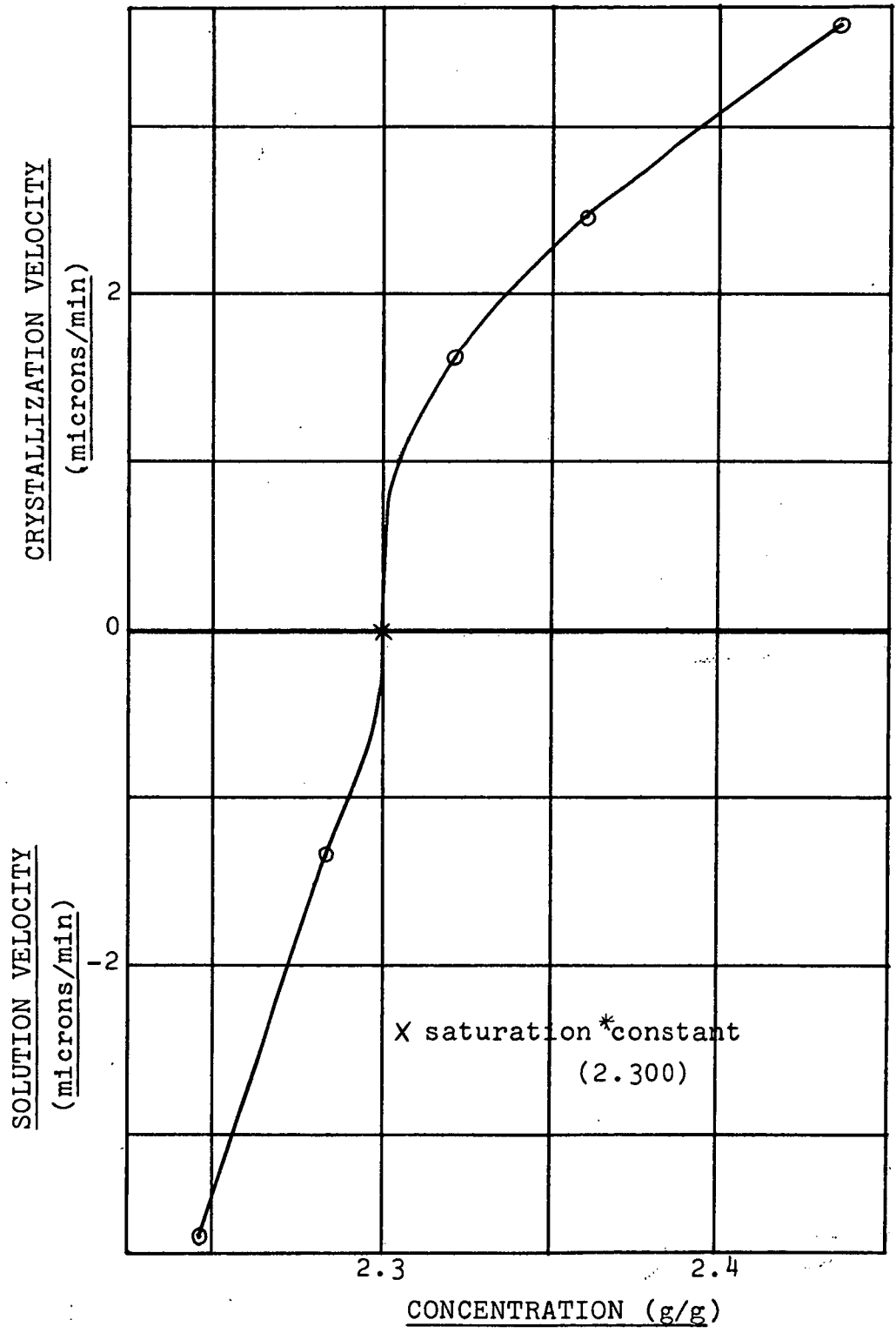
* concentration

Figure 4-2. CRYSTALLIZATION AND SOLUTION VELOCITIES
 V. CONCENTRATION AT 30°



* concentration

Figure 4-3. CRYSTALLIZATION AND SOLUTION VELOCITIES
 V. CONCENTRATION AT 40°



* concentration

Table 4-1. CRYSTALLIZATION VELOCITIES AND CONSTANTS.

Figures marked x belong also to Table 4-2.

<u>Temp.</u> °	<u>S.C.</u>	<u>S.C.</u>	<u>Sucrose Concn.</u>		<u>Cryst.</u>	<u>Constant</u>	<u>Constant</u>
	<u>Kelly</u>	<u>Tuck</u>	<u>g/g</u>	<u>%</u>	<u>Vel.</u>	<u>Kelly</u>	<u>Tuck</u>
20	x0.996	1.007	2.0111	66.790	0.80	x1.0	0.615
20	x0.999	1.010	2.0180	66.865	0.83	x8.3	0.415
20	1.008	1.019	2.0356	67.057	0.93	0.5637	0.2480
20	1.020	1.030	2.0587	67.306	0.99	0.2475	0.1623
20	1.080	1.092	2.1809	68.562	1.55	0.0957	0.0847
20	1.169	1.181	2.3597	70.235	2.12	0.0622	0.0586
20	1.268	1.281	2.5596	71.907	2.65	0.0490	0.0472
20	1.379	1.394	2.7849	73.579	3.09	0.0404	0.0393
20	1.506	1.522	3.0409	75.251	3.63	0.0355	0.0348
20	1.651	1.668	3.3335	76.924	4.10	0.0312	0.0307
20	1.819	1.838	3.6720	78.596	4.46	0.0270	0.0266
20	2.015	2.036	4.0679	80.268	5.53	0.0270	0.0267
30	x0.986	1.003	2.1356	68.108	0.70	x0.2258	0.8975
30	x0.993	1.010	2.1513	68.267	0.85	x0.5313	0.4047
30	1.013	1.030	2.1939	68.690	1.40	0.5187	0.2187
30	1.042	1.060	2.2578	69.305	2.04	0.2242	0.1594
30	1.093	1.104	2.3514	70.162	2.56	0.1391	0.1158
30	1.195	1.215	2.5887	72.134	3.74	0.0887	0.0815
30	1.286	1.300	2.7856	73.584	4.53	0.0732	0.0691
30	1.407	1.431	3.0478	75.295	5.43	0.0616	0.0592
30	1.546	1.572	3.3490	77.006	6.35	0.0537	0.0521
30	1.707	1.736	3.6988	78.718	7.59	0.0495	0.0484
30	1.897	1.929	4.1096	80.429	10.36	0.0533	0.0523
40	x0.985	1.010	2.3222	69.899	1.61	x0.4734	0.7319
40	1.002	1.027	2.3613	70.250	2.46	4.92	0.4033
40	1.034	1.060	2.4369	70.913	3.58	0.4420	0.2614
40	1.092	1.118	2.5722	72.007	5.07	0.2348	0.1864
40	1.193	1.222	2.8113	73.762	6.62	0.1455	0.1296

Table 4-1. CRYSTALLIZATION VELOCITIES AND CONSTANTS (cont'd).

Temp. °	S.C.	S.C.	Sucrose Concn.		Cryst.	Constant	Constant
	Kelly	Tuck	g/g	%	Vel.	Kelly	Tuck
40	1.309	1.341	3.0848	75.519	8.33	0.1143	0.1061
40	1.443	1.478	3.4004	77.275	9.93	0.0951	0.0903
40	1.600	1.639	3.7691	79.032	11.98	0.0848	0.0815
40	1.785	1.828	4.2053	80.789	15.47	0.0837	0.0812

Table 4-2. SOLUTION VELOCITIES AND CONSTANTS.

Temp. °	S.C.	S.C.	Sucrose Concn.		Soln.	Constant	Constant
	Kelly	Tuck	g/g	%	Vel.	Kelly	Tuck
20	0.863	0.872	1.7432	63.546	- 7.78	0.282	0.305
20	0.889	0.898	1.7944	64.214	- 5.80	0.258	0.284
20	0.915	0.925	1.8476	64.883	- 3.93	0.230	0.262
20	0.929	0.938	1.8751	65.218	- 3.01	0.209	0.245
20	0.936	0.945	1.8890	65.386	- 2.41	0.185	0.221
20	0.950	0.960	1.9181	65.731	- 1.79	0.177	0.224
20	0.971	0.981	1.9604	66.221	- 1.27	0.215	0.334
30	0.858	0.873	1.8594	65.028	-12.74	0.414	0.470
30	0.884	0.900	1.9165	65.712	- 9.61	0.384	0.451
30	0.904	0.920	1.9596	66.211	- 7.29	0.352	0.429
30	0.919	0.935	1.9911	66.568	- 5.36	0.305	0.386
30	0.940	0.957	2.0378	67.081	- 3.50	0.271	0.380
30	0.955	0.972	2.0697	67.423	- 2.36	0.243	0.393
30	0.970	0.987	2.1023	67.766	- 1.18	0.182	0.421
30	0.973	0.990	2.1089	67.834	- 1.01	0.174	0.481
40	0.852	0.872	2.0064	66.738	-23.32	0.666	0.793
40	0.879	0.901	2.0713	67.440	-16.75	0.588	0.732
40	0.894	0.915	2.1048	67.792	-12.95	0.516	0.664
40	0.908	0.930	2.1390	68.143	-10.09	0.465	0.627

Table 4-2. SOLUTION VELOCITIES AND CONSTANTS (cont'd).

<u>Temp.</u> °	<u>S.C.</u>	<u>S.C.</u>	<u>Sucrose Concn.</u>		<u>Soln.</u>	<u>Constant</u>	<u>Constant</u>
	<u>Kelly</u>	<u>Tuck</u>	<u>g/g</u>	<u>%</u>	<u>Vel.</u>	<u>Kelly</u>	<u>Tuck</u>
40	0.923	0.945	2.1739	68.493	- 7.59	0.417	0.602
40	0.938	0.961	2.2098	68.846	- 5.48	0.375	0.609
40	0.953	0.977	2.2463	69.196	- 3.59	0.326	0.664
40	0.970	0.993	2.2838	69.548	- 1.34	0.186	0.838

2. CRYSTALLIZATION AND SOLUTION CONSTANTS.

Both constants are calculated from the formula used to secure the crystallization constant in chapter 3,

$$n = k / (c - c_s) \quad (3-3) \quad \text{where } k \text{ is } \text{mg/m}^2/\text{min.}$$

The crystallization and solution constants inevitably vary with the solubility figures which happen to be taken as a basis. The Tuck solubility figures which have been determined from the velocities should, of course, yield the most consistent internal results as far as the constants are concerned, and the various plots confirm this (See especially Figures 4-7, 4-8 and 4-9).

The figures obtained for the crystallization and solution constants calculated to both Kelly and Tuck solubilities are also set out in Tables 4-1 and 4-2. The Kelly figures for solubility at 20°, 30° and 40° are 2.019, 2.167 and 2.356 g/g respectively.

Figures 4-4, 4-5 and 4-6 demonstrate the relationship between the crystallization constant and the saturation coefficient at 20°, 30° and 40° respectively. The plotting of the two sets of points for the two solubilities indicates little significance in the differences between the two sets.

Figure 4-4. CRYSTALLIZATION CONSTANT
V. SATURATION COEFFICIENT (20°)

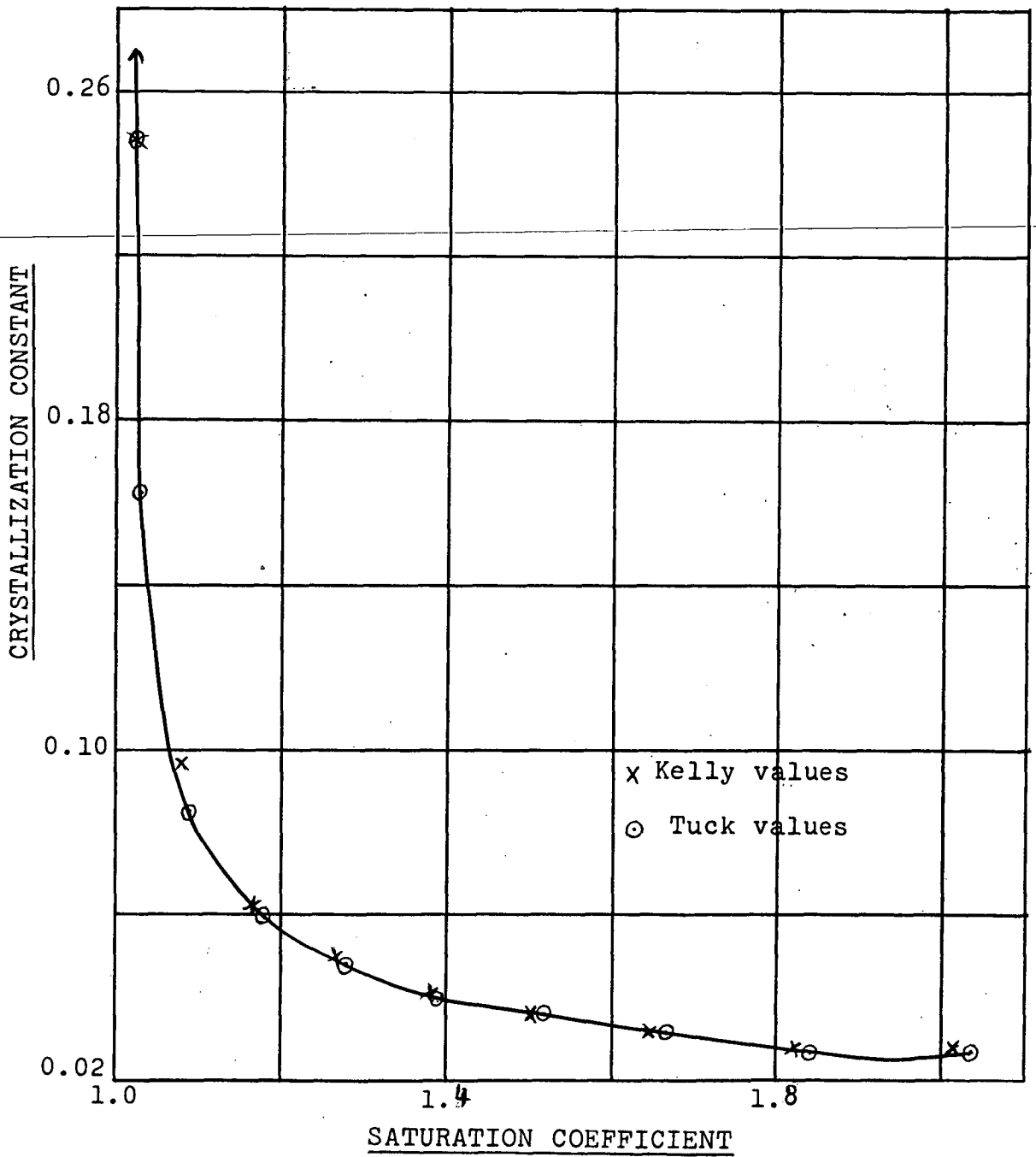


Figure 4-5. CRYSTALLIZATION CONSTANT
 V. SATURATION COEFFICIENT (30°)

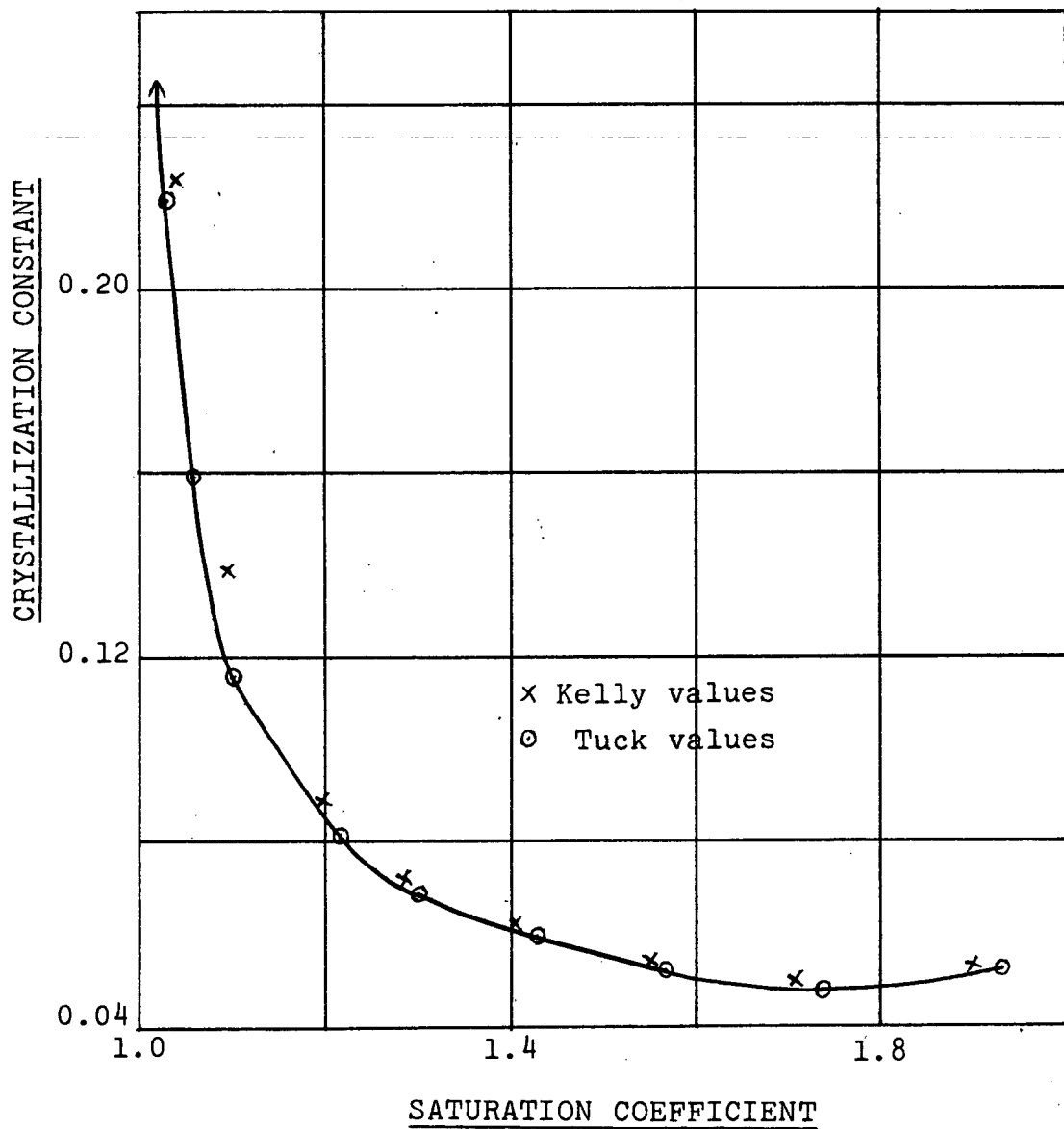
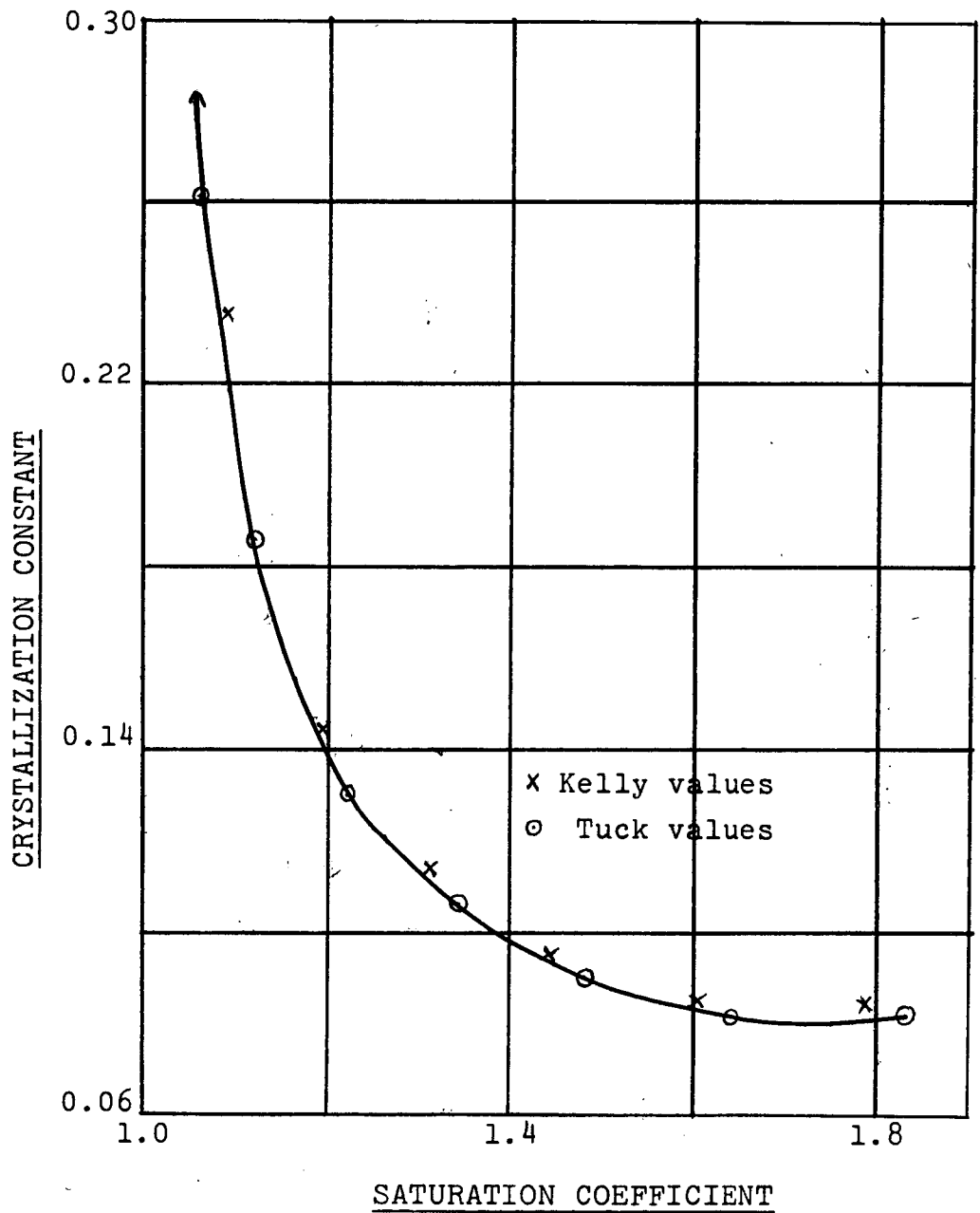


Figure 4-6. CRYSTALLIZATION CONSTANT
V. SATURATION COEFFICIENT (40°)



It is felt that the plots themselves are important to these studies since they show that the crystallization constant decreases with increasing concentration until a minimum is reached between $S = 1.70$ and 1.90 .

The other significant fact revealed by these plots is that the crystallization constant tends to infinity as the concentration tends to saturation ($S = 1.0$). This means, as Smythe¹ has pointed out, that the linear relationship (3-3) upon which the concept of the crystallization constant is based, breaks down at very low supersaturations. (The current studies indicate below about $S = 1.05$). At saturation, the crystallization velocity is by definition zero, the difference in concentrations is zero, nevertheless the crystallization constant ($= 0/0$) tends to infinity! In fact, the plots are only approximately linear for small regions, e.g. $S = 1.4-1.8$ at 20° ; $S = 1.3-1.6$ at 30° .

It is interesting to note that experimentally, using the refined technique, there was always a very slight change in weight in conditions of saturation. The crystal never reached the perfectly static position of constant weight in such a solution, but tended to oscillate between increase and decrease of weight. It was thus considered best to determine actual solubility values from the crystallization and solution velocities v . concentration plots, rather than from experimentally ascertaining where the increase or loss of weight of weight was negligible.

The relation between the solution constant and the saturation coefficient at 20° , 30° and 40° is illustrated in Figures 4-7, 4-8 and 4-9 respectively. The difference between the values based upon the different solubilities is significant and, as would be expected, the best plots are those based on the Tuck solubility figures which have themselves been determined in the current studies.

Figure 4-7. SOLUTION CONSTANT

V. SATURATION COEFFICIENT (20°)

X Kelly values

⊙ Tuck values

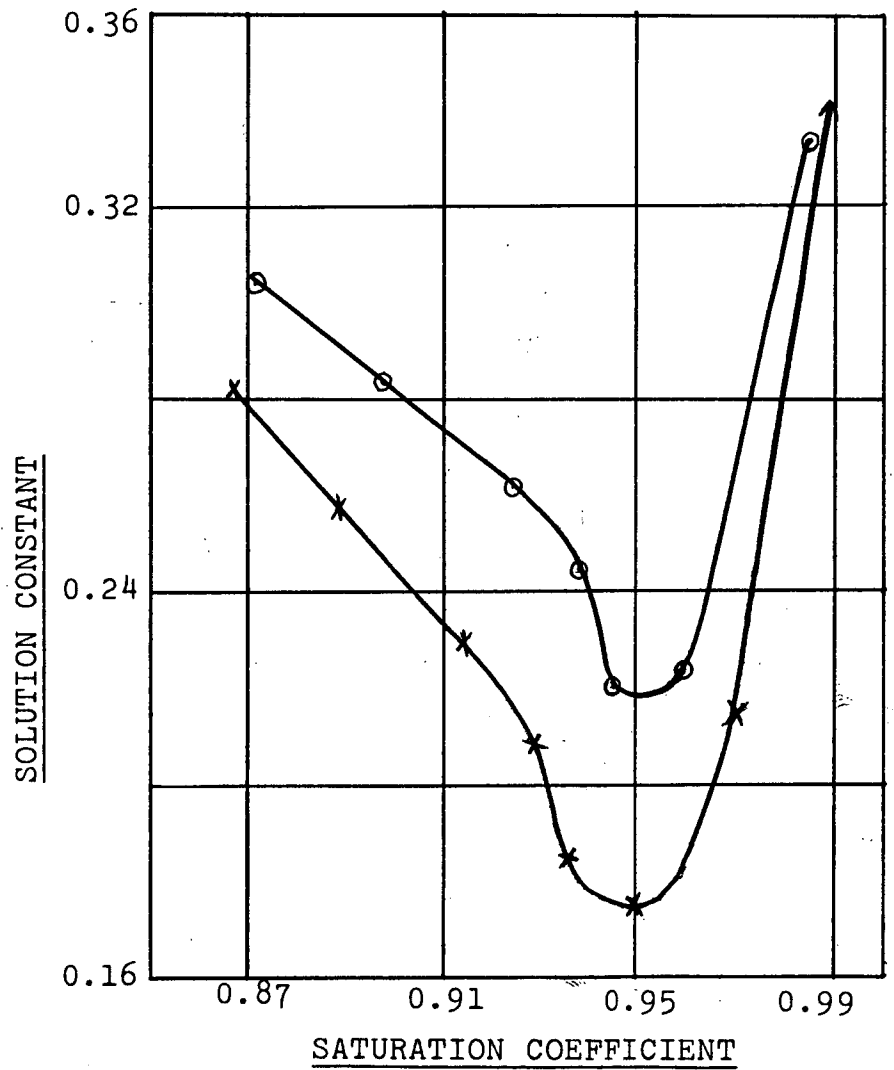


Figure 4-8. SOLUTION CONSTANT
 V. SATURATION COEFFICIENT (30°)

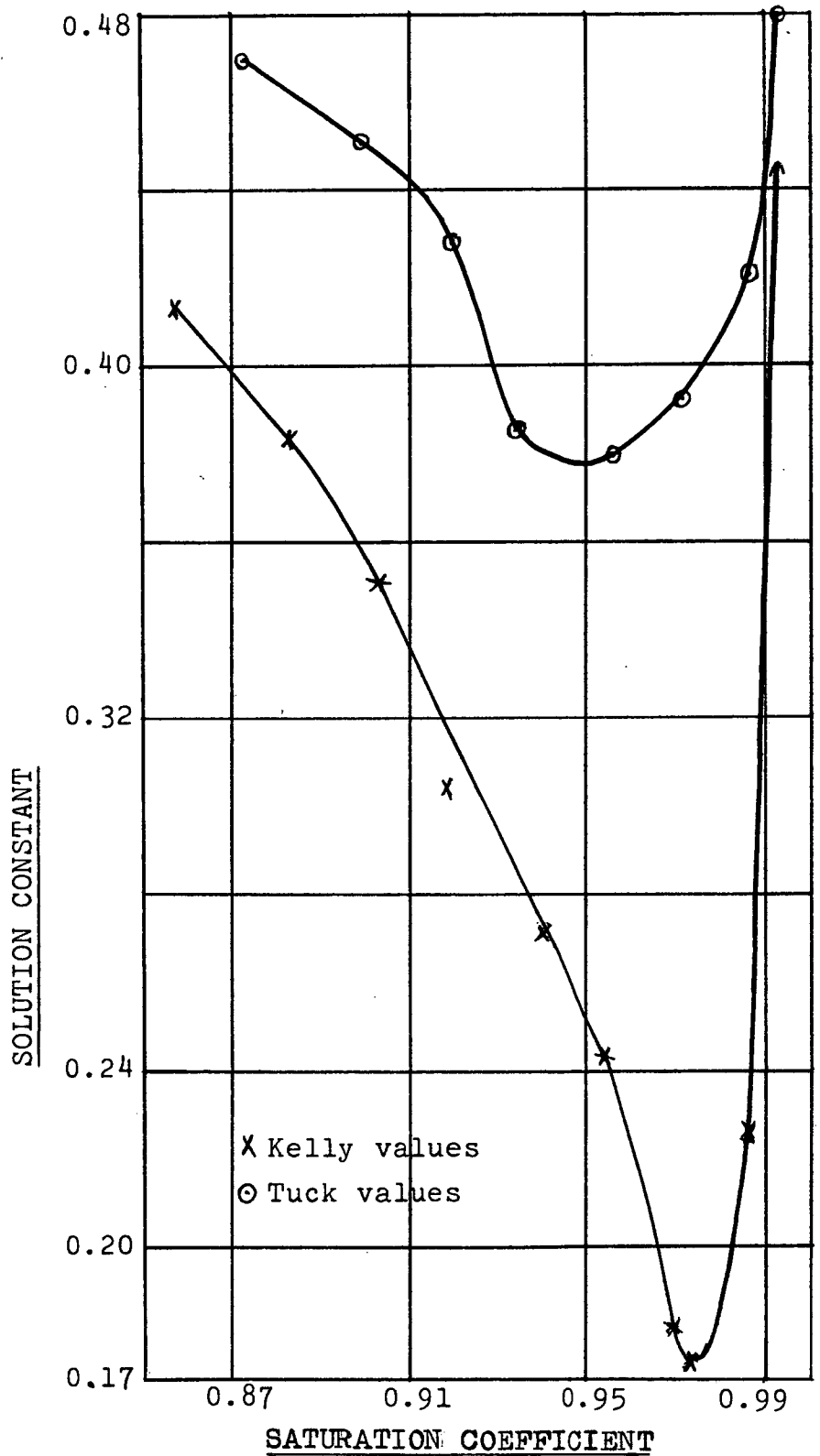
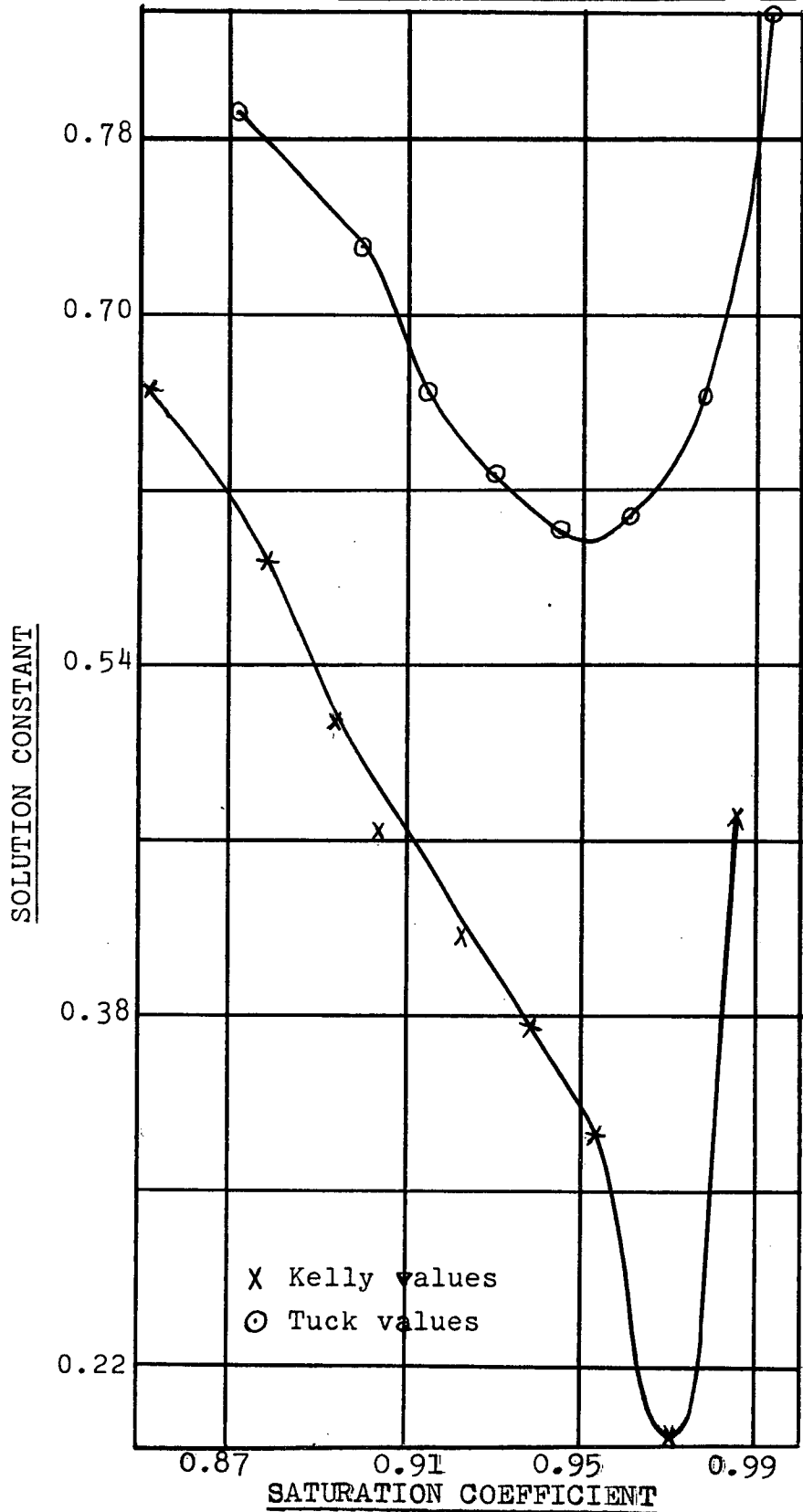


Figure 4-9. SOLUTION CONSTANT

V. SATURATION COEFFICIENT (40°)



The plots are comparable to a reverse of the crystallization constant v. saturation coefficient plots but with the minimum being reached much more rapidly at $S =$ approximately 0.95. Also the plots indicate that the solution constant tends to infinity at complete dilution. The minima appear to occur at approximately $n = 0.22$ (20°), 0.38 (30°) and 0.60 (40°). As in the case of crystal growth, the constant tends to infinity at saturation.

3. RATE EQUATIONS.

The basic equation* here for studying velocity of crystallization is:-

$$k = z (S - 1)^m e^{-Q/RT} \quad (4-3)$$

This may be put into the form,

$$\log k = a \log (S - 1) + b \quad (4-4)$$

Figures 4-10 and 4-11 indicate the relation between logarithms of the crystallization velocity and $(S - 1)$, the latter being calculated to both the Kelly and Tuck solubilities. The graphs reveal that the three plots are linear from approximately $S = 1.1$ to $S = 1.7$. Reference back to Figures 4-4, 4-5 and 4-6 shows that this is the region excluding high values of the crystallization constant at very low supersaturations and extending as far as the minimum value of the crystallization constant.

Making use of the plots, the velocity of crystallization was found to be:-

(a) With Kelly solubility:

$$k = 2.254 \times 10^7 (S - 1)^{0.505} e^{-8,915/RT} \quad (4-5)$$

(b) With Tuck solubility:

$$k = 6.498 \times 10^7 (S - 1)^{0.485} e^{-9,555/RT} \quad (4-6)$$

This latter rate equation was tested for degree of fit and Table 4-3 records the standard deviation calculations.

* Replace "here" by "used here, having been suggested by Kelly³"

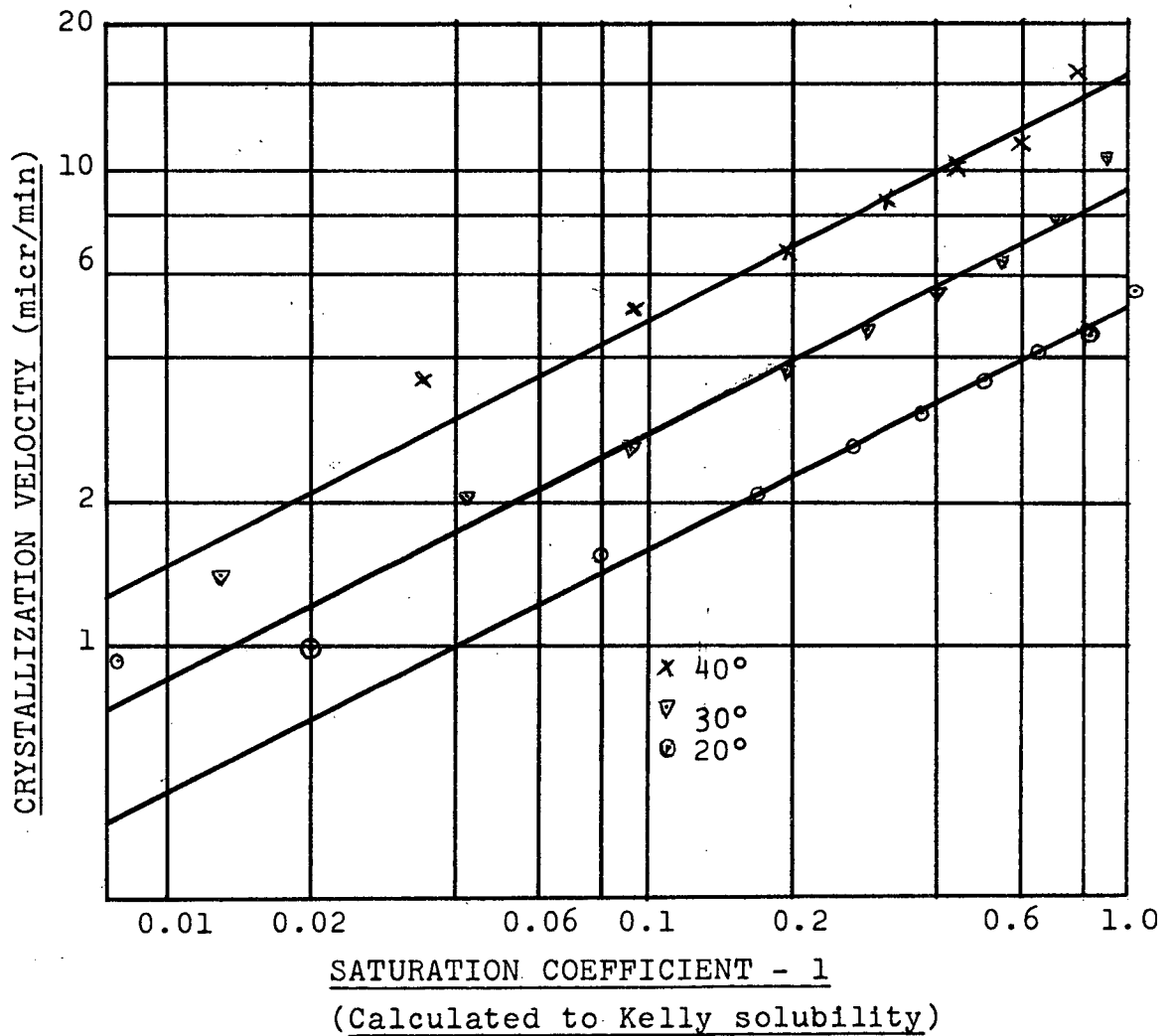
Figure 4-10. LOG CRYSTALLIZATION VELOCITYV. LOG (S - 1)(S calculated to Kelly solubility)

Figure 4-11. LOG CRYSTALLIZATION VELOCITY

V. LOG (S - 1)

(S calculated to Tuck solubility)

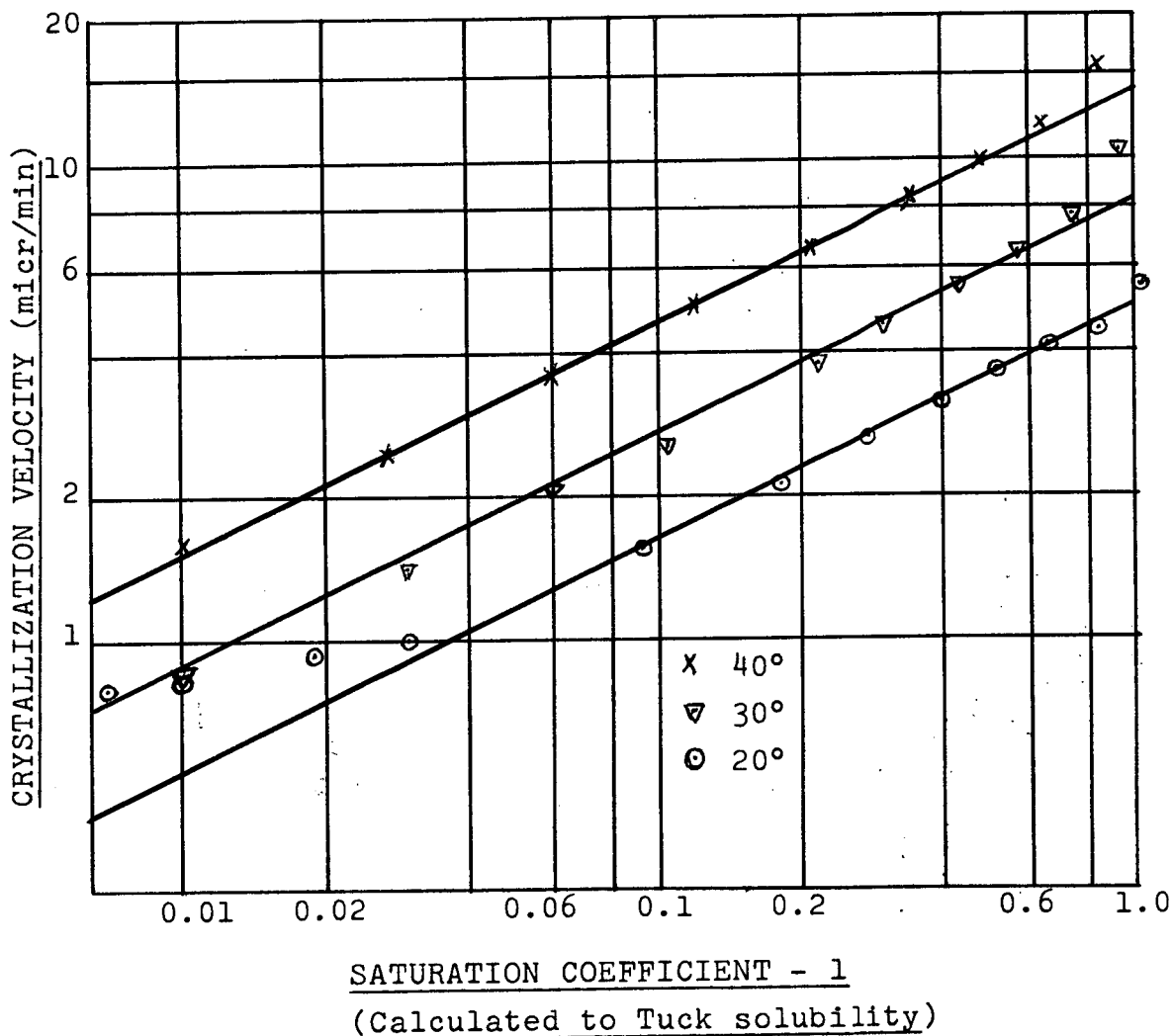


Table 4-3. CALCULATION OF STANDARD DEVIATION OF CRYSTALLIZATION VELOCITY DATA FROM EQUATION (4-6).

t°	k_{obs}	k_{calc}	Δk	$10^2(\Delta k/k_{obs})$	$10^4(\Delta k/k_{obs})^2$	<u>S - 1</u>
20	0.80	0.44	0.36	45.00	2024.9	0.007
20	0.83	0.52	0.31	37.35	1395.1	0.010
20	0.93	0.72	0.21	22.58	509.8	0.019
20	0.99	0.89	0.10	10.00	100.0	0.030
20	1.55	1.54	0.01	0.65	0.42	0.092
20	2.12	2.13	0.01	0.47	0.22	0.181
20	2.65	2.64	0.01	0.38	0.14	0.281
20	3.09	3.11	0.02	0.64	0.42	0.394
20	3.63	3.57	0.06	1.65	2.73	0.522
20	4.10	4.02	0.08	1.95	3.81	0.668
20	4.46	4.48	0.02	0.45	0.20	0.838
20	5.53	4.97	0.56	10.13	102.6	1.036

Standard Deviation (omitting the first four and the last experiments as being obviously not consistent with this mathematical treatment) = 1.07%.

t°	k_{obs}	k_{calc}	Δk	$10^2(\Delta k/k_{obs})$	$10^4(\Delta k/k_{obs})^2$	<u>S - 1</u>
30	0.70	0.50	0.20	28.57	816.2	0.003
30	0.85	0.90	0.05	5.88	34.58	0.010
30	1.40	1.53	0.13	9.29	86.22	0.030
30	2.04	2.15	0.11	5.39	29.08	0.060
30	2.56	2.80	0.24	9.38	87.90	0.104
30	3.74	3.98	0.24	6.42	41.18	0.215
30	4.53	4.68	0.15	3.31	10.96	0.300
30	5.43	5.58	0.15	2.76	7.63	0.431
30	6.35	6.40	0.05	0.79	00.62	0.572
30	7.59	7.24	0.35	4.61	21.28	0.736
30	10.36	8.10	2.26	21.82	476.0	0.929

Table 4-3. CALCULATION OF STANDARD DEVIATION OF CRYSTALLIZATION VELOCITY DATA FROM EQUATION (4-6) (cont'd).

Standard Deviation (omitting first and last experiments) = 5.96%						
<u>t°</u>	<u>k_{obs}</u>	<u>k_{calc}</u>	<u>Δk</u>	<u>10²(Δk/k_{obs})</u>	<u>10⁴(Δk/k_{obs})²</u>	<u>S - 1</u>
40	1.61	1.49	0.12	7.45	55.57	0.010
40	2.46	2.42	0.04	1.63	2.65	0.027
40	3.58	3.56	0.02	0.56	0.31	0.060
40	5.07	4.94	0.13	2.56	6.57	0.118
40	6.62	6.71	0.09	1.36	1.85	0.222
40	8.33	8.27	0.06	0.72	0.52	0.341
40	9.93	9.74	0.19	1.91	3.66	0.478
40	11.98	11.21	0.77	6.43	41.30	0.639
40	15.47	12.71	2.76	17.84	318.3	0.828
Standard Deviation (omitting first and last two experiments) = 1.61%.						
Standard Deviation over the three temperatures = 4.01%						

The greater deviation at 30° may perhaps be explained by the fact that the equation (4-6) was actually calculated using the 20° and 40° plots.

The corresponding basic equation for solution rate is,

$$k = -z(1 - S)^m e^{-Q/RT} \quad (4-7)$$

Figures 4-12 and 4-13 show the relation between logarithms of the solution velocity and (1 - S) calculated to Kelly and Tuck solubilities. It is apparent that the plots are linear except for the region where S is greater than approximately 0.95. It is significant that in the solution constant v. saturation coefficient plots (Figures 4-7, 4-8 and 4-9), the minimum occurs at about S = 0.95, and the solution constant increases very rapidly from S = 0.97 to S = 1.0.

Figure 4-12. LOG SOLUTION VELOCITY
 V. LOG (1 - S)
 (S calculated to Kelly solubility)

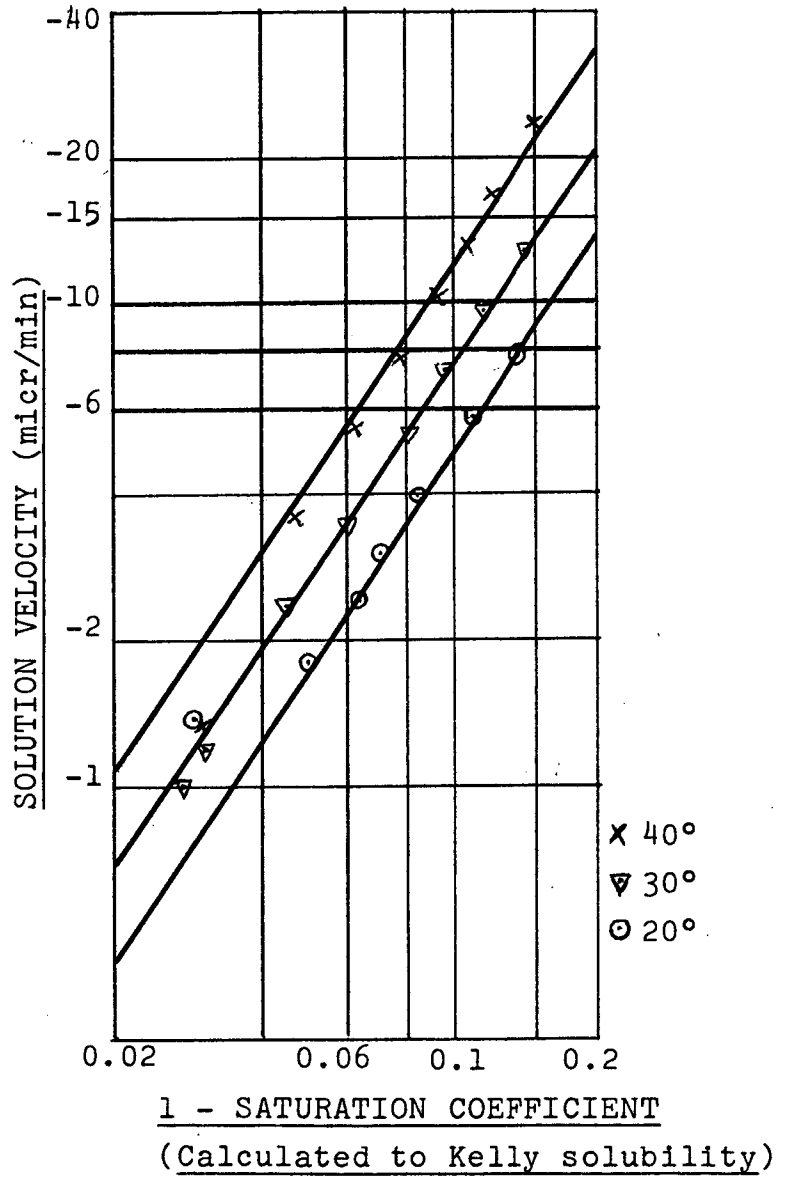
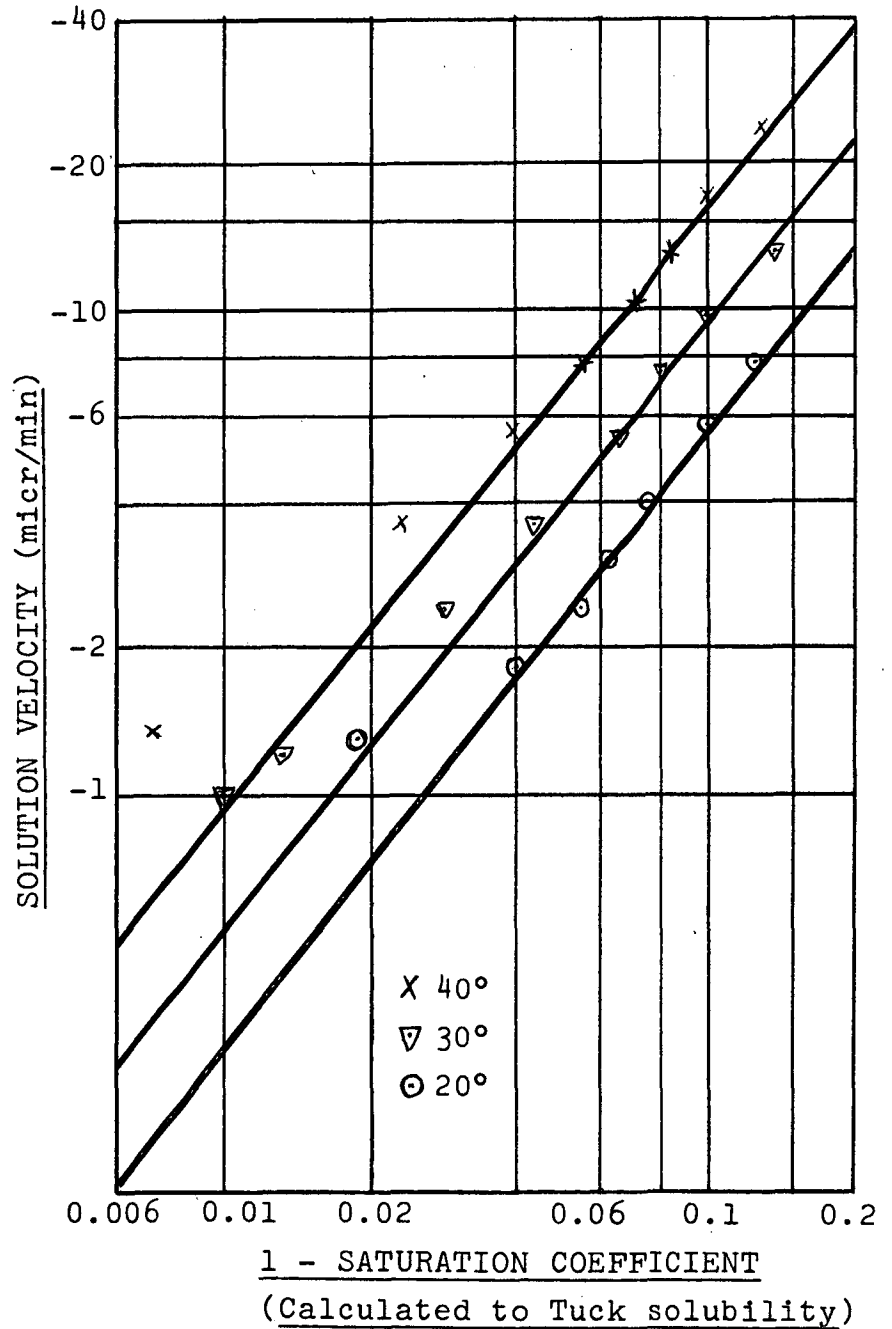


Figure 4-13. LOG SOLUTION VELOCITY
V. LOG (1 - S)
 (S calculated to Tuck solubility)



The solution velocity was calculated and the following results obtained:-

(a) With Kelly solubility:

$$k = - 1.631 \times 10^8 (1 - S)^{1.5} e^{-8,090/RT} \quad (4-8)$$

(b) With Tuck solubility:

$$k = - 2.393 \times 10^9 (1 - S)^{1.26} e^{-9,906/RT} \quad (4-9)$$

Equation (4-9) was tested for degree of fit and Table 4-4 records the calculation.

Table 4-4. CALCULATION OF STANDARD DEVIATION OF SOLUTION VELOCITY DATA FROM EQUATION (4-9).

t°	k_{obs}	k_{calc}	Δk	$\frac{(\Delta k/k_{obs})10^2}{}$	$\frac{(\Delta k/k_{obs})^2 10^4}{}$	$1 - S$
20	-1.27	-0.67	-0.60	47.26	2233	0.019
20	-1.79	-1.71	-0.08	4.47	19.97	0.040
20	-2.41	-2.55	-0.14	5.81	33.75	0.055
20	-3.01	-2.96	-0.05	1.66	2.76	0.062
20	-3.93	-3.77	-0.16	4.07	16.57	0.075
20	-5.80	-5.55	-0.25	4.31	18.58	0.102
20	-7.78	-7.43	-0.35	4.50	20.24	0.128
Standard Deviation (excluding the first experiment) = 4.32%.						
t°	k_{obs}	k_{calc}	Δk	$\frac{(\Delta k/k_{obs})10^2}{}$	$\frac{(\Delta k/k_{obs})^2 10^4}{}$	$1 - S$
30	-1.01	-0.52	-0.49	48.52	2354	0.010
30	-1.18	-0.73	-0.45	38.14	1454	0.013
30	-2.36	-1.91	-0.45	19.07	363.6	0.028
30	-3.50	-3.28	-0.22	6.29	39.50	0.043
30	-5.36	-5.51	-0.15	2.80	7.83	0.065
30	-7.29	-7.16	-0.13	1.78	3.18	0.080
30	-9.61	-9.49	-0.12	1.25	1.56	0.100
30	-12.74	-12.82	-0.08	0.71	0.50	0.127

Table 4-4. CALCULATION OF STANDARD DEVIATION OF SOLUTION VELOCITY DATA FROM EQUATION (4-9) (cont'd).

Standard Deviation (excluding first three experiments) = 3.24%.						
<u>t°</u>	<u>k_{obs}</u>	<u>k_{calc}</u>	<u>Δk</u>	<u>(Δk/k_{obs})10²</u>	<u>(Δk/k_{obs})²10⁴</u>	<u>1 - S</u>
40	- 1.34	- 0.56	-0.78	58.22	3388.5	0.007
40	- 3.59	- 2.52	-1.07	29.81	888.5	0.023
40	- 5.48	-4.90	-0.58	10.58	112.0	0.039
40	- 7.59	-7.54	-0.05	0.66	0.43	0.055
40	-10.09	-10.23	-0.14	1.39	1.93	0.070
40	-12.95	-13.07	-0.12	0.93	0.86	0.085
40	-16.75	-15.84	-0.91	5.43	29.52	0.099
40	-23.32	-21.89	-1.43	6.13	37.59	0.128
Standard Deviation (excluding first three experiments) = 3.75%.						
Standard Deviation over the three temperatures = 3.83%.						

4. COMPARISON OF THE CURRENT CRYSTALLIZATION STUDIES WITH THOSE OF KUCHARENKO AND SMYTHE.

(a) KUCHARENKO: It is important to consider the work of Kucharenko² who is regarded as the pioneer in this field. Kucharenko used large (2-12 g) crystals and grew them in large excess of supersaturated sucrose solutions.

In changing the crystallization velocity unit to microns per minute, equations (4-1) and (4-2) have been utilised, assuming growth over one hour, and average crystal weight of 7 g. The increase in weight of the crystal was calculated from Kucharenko's own equation,

$$k = 10^6 \times \Delta p / 4.12 \times p^{2/3} \times \theta \quad \text{mg/m}^2/\text{min.} \quad (4-10)$$

Table 4-5 sets out the crystallization rates and constants for the three temperatures especially considered in this chapter. S and the constants are calculated to Kelly and Tuck solubilities.

Table 4-5. KUCHARENKO CRYSTALLIZATION VELOCITIES AND CONSTANTS.

<u>Temp.</u> °	<u>Concn.</u> g/g	<u>S.C.</u> <u>Kelly</u>	<u>S.C.</u> <u>Tuck</u>	<u>Velocity</u> <u>micr/min</u>	<u>Constant</u> <u>Kelly</u>	<u>Constant</u> <u>Tuck</u>
20	2.070	1.025	1.034	0.07	0.0138	0.0097
20	2.102	1.041	1.052	0.12	0.0145	0.0115
20	2.134	1.057	1.068	0.18	0.0157	0.0132
20	2.168	1.074	1.085	0.22	0.0148	0.0129
20	2.202	1.091	1.102	0.28	0.0153	0.0137
20	2.237	1.108	1.120	0.34	0.0156	0.0142
20	2.272	1.125	1.137	0.40	0.0158	0.0146
20	2.308	1.143	1.155	0.46	0.0159	0.0148
20	2.346	1.162	1.174	0.53	0.0162	0.0152
20	2.384	1.181	1.193	0.61	0.0167	0.0158
20	2.422	1.200	1.212	0.70	0.0174	0.0165
20	2.462	1.219	1.232	0.76	0.0172	0.0164
20	2.503	1.240	1.253	0.84	0.0174	0.0166
20	2.544	1.260	1.273	0.90	0.0171	0.0164
30	2.231	1.030	1.048	0.11	0.0172	0.0109
30	2.267	1.046	1.064	0.22	0.0220	0.0161
30	2.304	1.063	1.081	0.37	0.0270	0.0213
30	2.342	1.081	1.099	0.56	0.0320	0.0264
30	2.380	1.098	1.118	0.72	0.0338	0.0288
30	2.420	1.117	1.137	0.91	0.0360	0.0314
30	2.461	1.136	1.156	1.11	0.0378	0.0335
30	2.502	1.155	1.175	1.33	0.0397	0.0358
30	2.545	1.175	1.195	1.63	0.0431	0.0393
30	2.589	1.195	1.216	1.93	0.0457	0.0421
40	2.421	1.027	1.053	0.21	0.0323	0.0174
40	2.463	1.045	1.071	0.42	0.0393	0.0258
40	2.506	1.064	1.091	0.72	0.0480	0.0350
40	2.550	1.082	1.109	0.99	0.0510	0.0396

Table 4-5. KUCHARENKO CRYSTALLIZATION RATES AND CONSTANTS (cont'd)

<u>Temp.</u> °	<u>Concn.</u> g/g	<u>S.C.</u> <u>Kelly</u>	<u>S.C.</u> <u>Tuck</u>	<u>Velocity</u> <u>micr/min</u>	<u>Constant</u> <u>Kelly</u>	<u>Constant</u> <u>Tuck</u>
40	2.595	1.101	1.129	1.25	0.0523	0.0424
40	2.641	1.121	1.149	1.54	0.0540	0.0452
40	2.688	1.141	1.169	1.90	0.0571	0.0489
40	2.737	1.162	1.190	2.25	0.0591	0.0515
40	2.786	1.182	1.211	2.63	0.0612	0.0541
40	2.837	1.204	1.234	3.00	0.0624	0.0559
40	2.890	1.227	1.257	3.77	0.0706	0.0639

The Kucharenko rates are very much lower than those obtained in the current studies, especially for the lower supersaturations. The values in microns / minute range from 0.07 to 0.90 at 20°, 0.11 to 1.93 at 30°, and 0.21 to 3.77 at 40°, whereas the Tuck values extend from (approximately) 1.05 to 2.60 (20°), 1.18 to 3.74 (30°) and 3.35 to 7.10 (40°) for the same concentration range. This is discussed in detail later under section (b).

It is interesting to note that Kucharenko's crystallization constant increases with increasing concentration (See Figure 4-14) (The slopes of the 30° and 40° plots are approximately the same.) This has doubtless influenced thought on the subject giving the impression that this is a fact. However, Kucharenko's studies do not take in the concentration range of the current studies with readings nearer saturation and with higher concentrations reaching up to $S = 1.8-2.0$.

The relationship between crystallization velocity and concentration (g/g) in the Kucharenko results is illustrated in Figure 4-15 which is drawn to the same scale as the Tuck plots (Figures 4-1, 4-2 and 4-3). Substantial difference is evident, especially at 20°.

Figure 4-14. CRYSTALLIZATION CONSTANT
V. SATURATION COEFFICIENT
(KUCHARENKO)

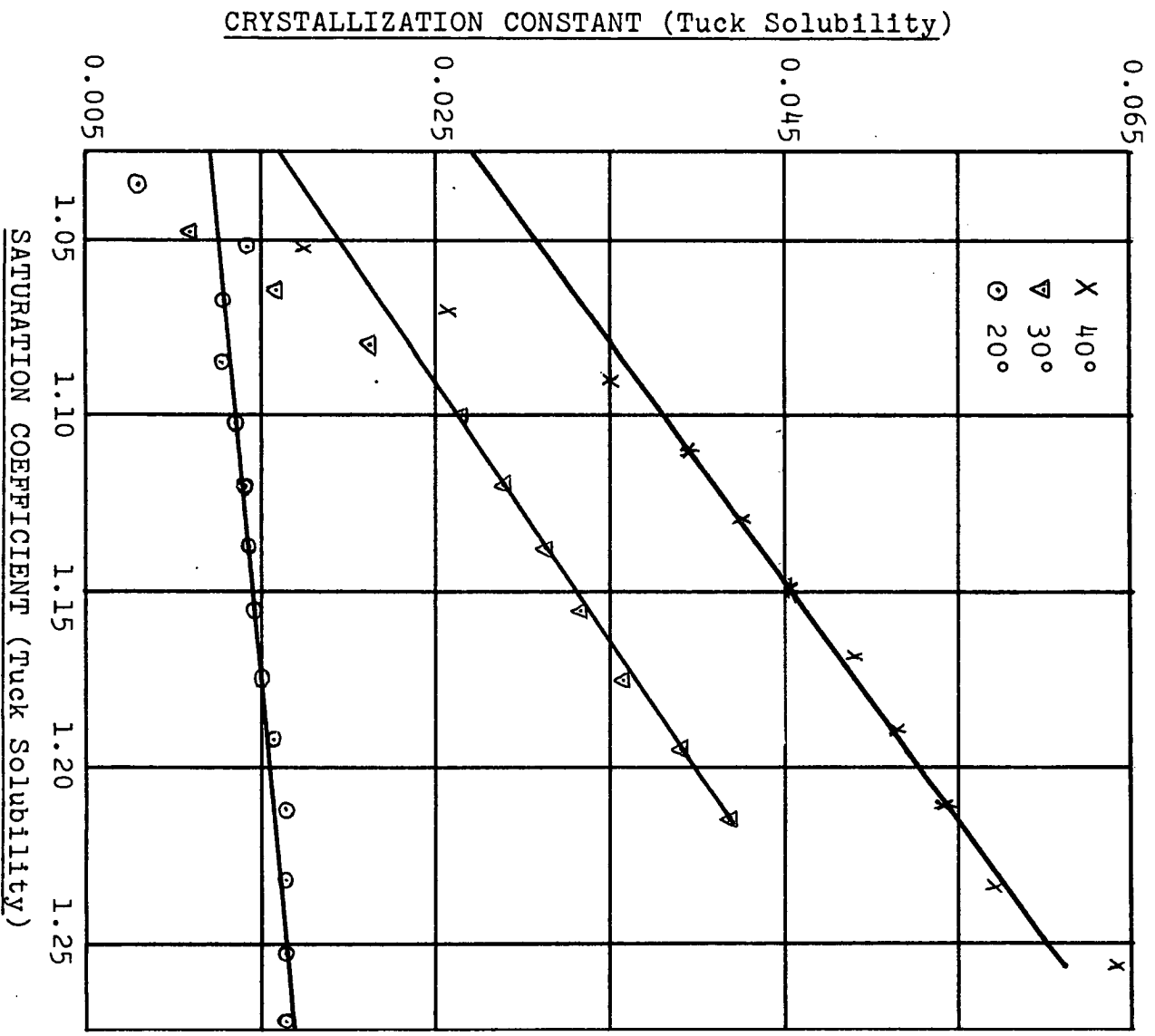
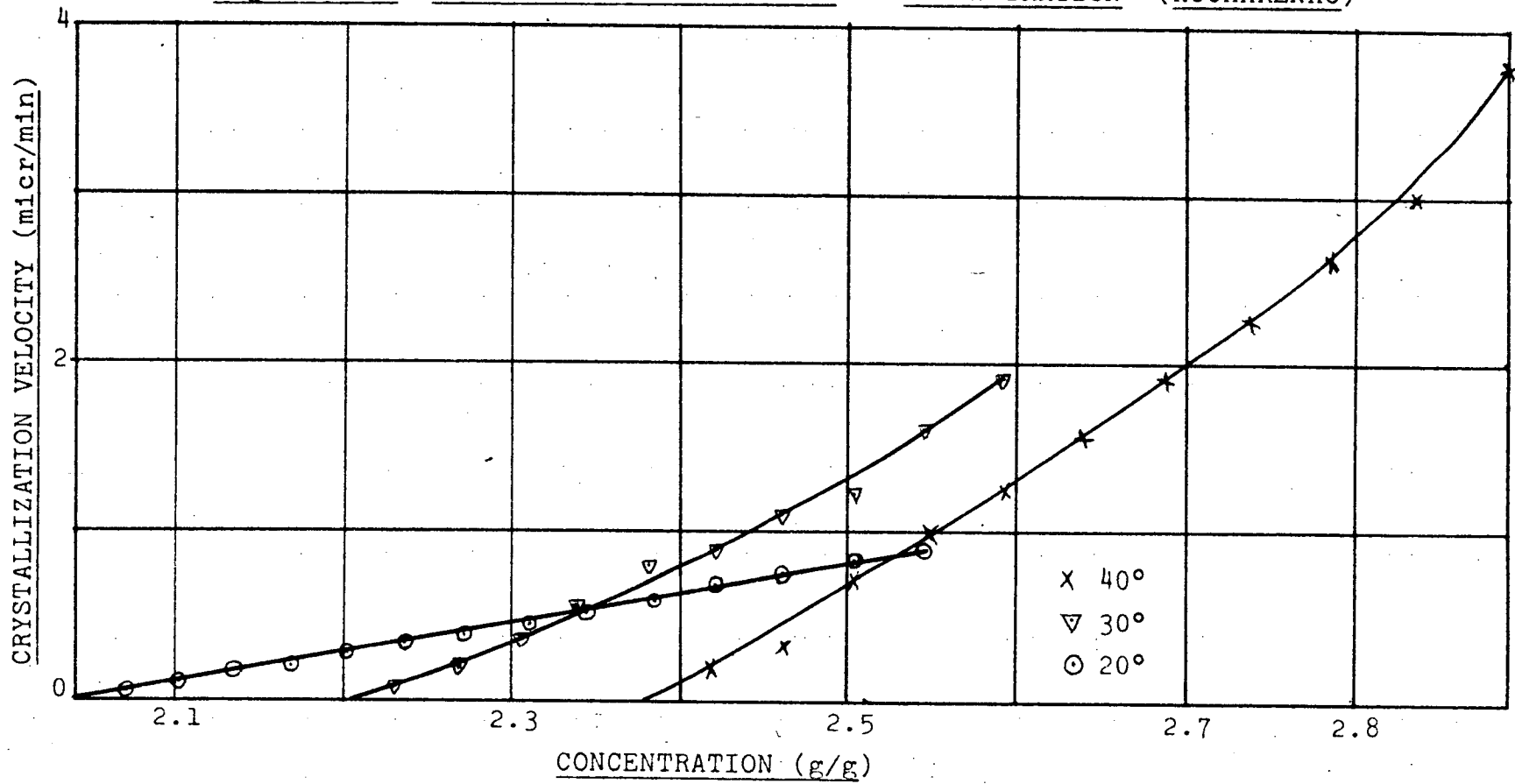


Figure 4-15. CRYSTALLIZATION VELOCITY V. CONCENTRATION (KUCHARENKO)



For the Kucharenko data, log crystallization velocity v. log (S - 1) with S being calculated to Tuck solubility, data are plotted in Figure 4-16. The rate equation calculated from these values is as follows:-

$$k = 2.419 \times 10^7 (S - 1)^{1.6} e^{-9,658/RT} \quad (4-11)$$

This equation was tested for degree of fit as in Table 4-3. The 20° results fitted poorly with a standard deviation of 48.65%. However, the 30° and 40° figures, from which the equation was calculated, had standard deviations of 3.60% and 4.09% respectively. The first two experiments were discarded in each case as being obviously not consistent with this mathematical treatment.

The standard deviation over both 30° and 40° was 3.87%, but over the three temperatures was 33.04%. As the velocities recorded were small, the degree of fit in the cases of the 30° and 40° results was good. However, it is not easy to explain how the 20° values from S = 1.1 became so much lower than the rate equation values. Kelly³ has demonstrated that Kucharenko's crystallization results at 50°, 60° and 70° closely parallel those at 30° and 40° in a plot of log crystallization velocity v. log (S - 1), S being calculated to Herzfeld solubility.

(b) SMYTHE: Smythe's earlier crystallization studies¹ have already been mentioned in chapters 1 and 3. However, since the current studies were undertaken, Smythe⁴ has described further studies which were carried out at 21°, 31° and 41°.

Smythe measured increase in weight over one hour, and used crystals weighing between 40 and 150 mg as previously. His crystallization velocities have been converted to microns / min. by means of equations (4-1), (4-2) and (4-10). Crystal weight was taken as the average weight, i.e. 95 mg.

Figure 4-16. LOG CRYSTALLIZATION VELOCITY

V. LOG (S - 1)

(KUCHARENKO)

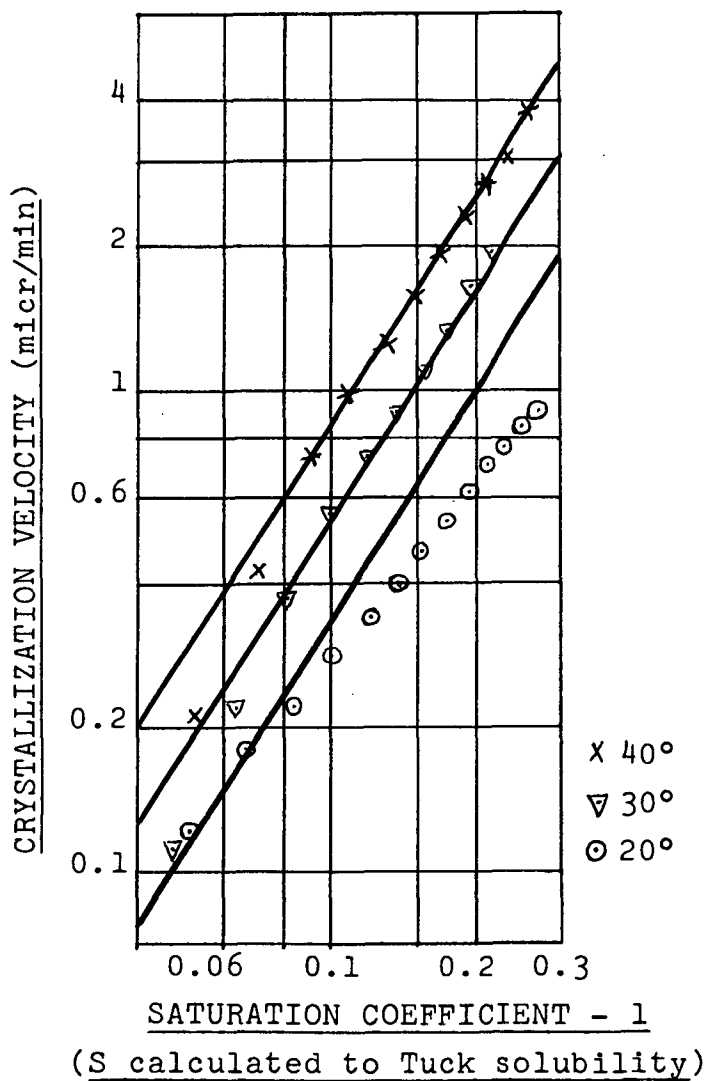


Table 4-6 presents Smythe's crystallization rates and constants. The saturation coefficient has been calculated to both Kelly and Tuck solubilities, while the crystallization constant is only calculated to Kelly solubility. The Kelly solubility values are 2.033, 2.184 and 2.377 (g/g) at 21°, 31° and 41° respectively, with Tuck solubility figures being 2.009, 2.145 and 2.320 (g/g) for the same temperatures. These latter values are obtained from the quadratic equation derived from the Tuck solubilities at 20°, 30° and 40° (See Table 4-7).

Table 4-6. SMYTHE CRYSTALLIZATION VELOCITIES AND CONSTANTS.

<u>Temp.</u> °	<u>Concn.</u> g/g	<u>S.C.</u> <u>Kelly</u>	<u>S.C.</u> <u>Tuck</u>	<u>Velocity</u> <u>micr/min</u>	<u>Constant</u> <u>Kelly</u>
21	2.077	1.022	1.034	0.11	0.0250
21	2.096	1.031	1.044	x0.16	0.0254
21	2.115	1.040	1.053	x0.16	0.0195
21	2.145	1.055	1.068	0.24	0.0214
21	2.195	1.080	1.093	x0.40	0.0247
21	2.210	1.087	1.110	0.41	0.0232
21	2.241	1.102	1.116	0.47	0.0226
21	2.311	1.137	1.151	0.65	0.0234
21	2.333	1.147	1.162	0.70	0.0233
21	2.442	1.201	1.216	0.98	0.0240
21	2.472	1.216	1.232	1.04	0.0237
21	2.546	1.252	1.268	1.20	0.0234
21	2.636	1.296	1.313	1.36	0.0226
21	2.643	1.300	1.317	1.47	0.0241
21	2.697	1.326	1.343	x1.37	0.0206
21	2.711	1.333	1.350	x1.42	0.0209
21	2.738	1.347	1.364	x1.46	0.0207
21	2.831	1.392	1.409	1.78	0.0223
21	2.846	1.400	1.417	x1.74	0.0214

Table 4-6. SMYTHE CRYSTALLIZATION VELOCITIES AND CONSTANTS (cont'd)

<u>Temp.</u> °	<u>Concn.</u> g/g	<u>S.C.</u> Kelly	<u>S.C.</u> Tuck	<u>Velocity</u> micr/min	<u>Constant</u> Kelly
31	2.221	1.017	1.036	0.24	0.0649
31	2.231	1.022	1.041	0.29	0.0636
31	2.273	1.041	1.060	0.47	0.0528
31	2.311	1.058	1.077	0.60	0.0473
31	2.497	1.143	1.164	1.63	0.0521
31	2.623	1.201	1.223	2.18	0.0497
31	2.711	1.241	1.264	2.47	0.0469
31	2.861	1.311	1.334	3.61	0.0533
31	3.000	1.374	1.398	4.04	0.0495
41	2.378	1.00004	1.025	x0.06	0.60
41	2.390	1.005	1.030	x0.12	0.092
41	2.425	1.020	1.045	x0.61	0.127
41	2.454	1.032	1.057	x0.72	0.094
41	2.460	1.035	1.060	0.98	0.118
41	2.478	1.042	1.067	x0.89	0.088
41	2.478	1.042	1.067	1.13	0.112
41	2.509	1.056	1.082	x1.39	0.105
41	2.509	1.056	1.082	1.58	0.117
41	2.515	1.058	1.084	1.39	0.101
41	2.571	1.082	1.108	x2.35	0.121
41	2.571	1.082	1.108	2.24	0.115
41	2.623	1.103	1.130	2.76	0.112
41	2.745	1.155	1.183	x4.17	0.113
41	2.745	1.155	1.183	4.08	0.111
41	2.831	1.191	1.220	4.88	0.107
41	2.976	1.252	1.282	7.11	0.119
41	3.024	1.272	1.303	7.28	0.113
41	3.082	1.297	1.328	8.21	0.116
41	3.124	1.314	1.346	x7.86	0.105
41	3.141	1.321	1.353	8.29	0.109

The relationships between the crystallization constant and the saturation coefficient (both calculated to Kelly solubility) for the Smythe data, are illustrated in Figure 4-17, and crystallization velocity is plotted against concentration in Figure 4-18.

The Smythe data enable solubilities to be estimated by extrapolation, and give values very close to those reported by Kelly. These figures are 2.035, 2.184 and 2.372 (g/g) at 21°, 31° and 41° respectively. It was therefore felt that the Kelly rather than the Tuck solubilities would provide the best values for calculation of the crystallization constant from the Smythe data.

The three plots in Figure 4-17 appear to be approximately linear, with the crystallization constant very slightly decreasing with increasing concentration, except in the 21° plot in which values at very low supersaturations (i.e. below $S = 1.06$) show a wide scatter. The first 41° experiment is rejected from the point of view of the crystallization constant since the concentration is so near to the Kelly solubility. Although the Smythe solubility would give a more realistic figure for the constant at this point (0.10), even this is no greater than the constant for the third 41° experiment using the Smythe solubility (0.115). It is therefore clear that there is no advantage in changing from the Kelly to Smythe solubilities.

Only the first two experiments of the 31° set suggest that the crystallization constant could substantially increase as S tends to 1.0. In fact, the 41° results at very low supersaturations (i.e. below $S = 1.06$) extend from $n = 0.127$ to $n = 0.088$. The scatter of results when so treated is believed to be related to the likelihood that a reading over one hour under such conditions could differ significantly from a reading over 45 minutes. In the light of the current experiments it is considered that the latter would give a more

Figure 4-17. CRYSTALLIZATION CONSTANT
V. SATURATION COEFFICIENT
(SMYTHE)

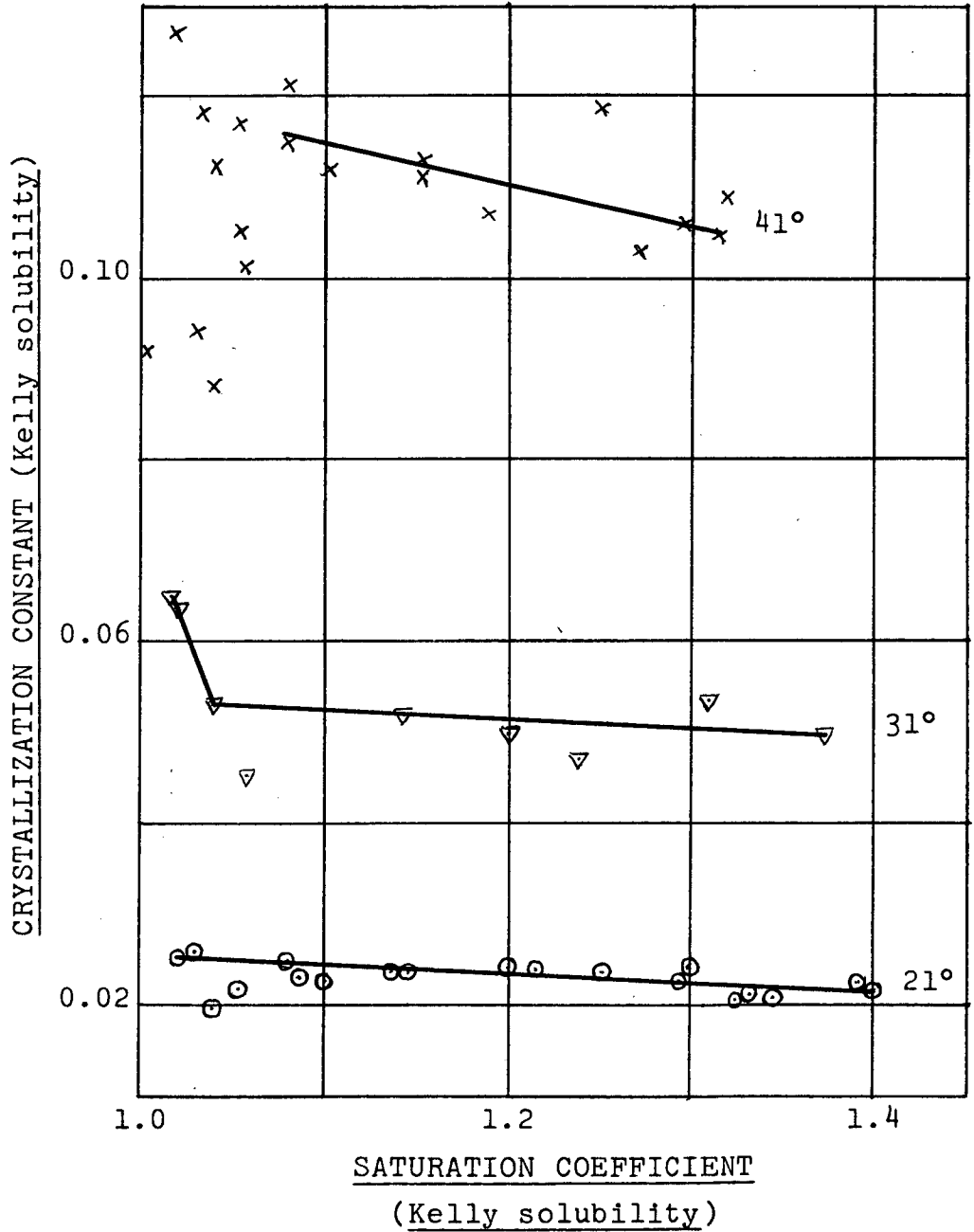
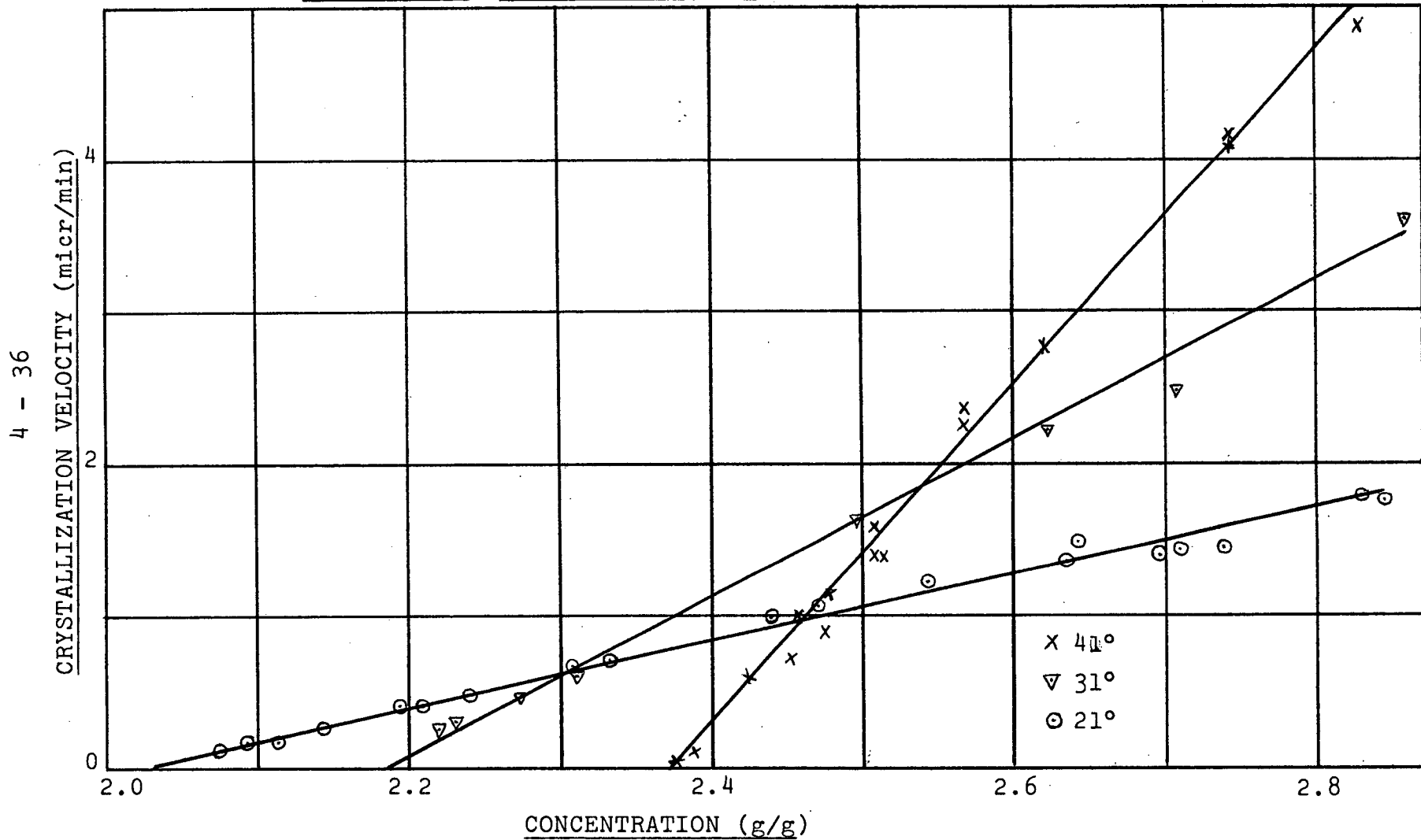


Figure 4-18. CRYSTALLIZATION VELOCITY V. CONCENTRATION (SMYTHE)



accurate crystallization velocity value.

It is to be noted that the Smythe results do not have a higher concentration than S (Kelly) = 1.40, 1.375 and 1.325 at 21°, 31° and 41° respectively. According to the current studies at 20°, 30° and 40°, it was only at approximately S (Kelly) = 1.785-2.015 that the crystallization constant began to slowly increase.

The velocity plots of Figure 4-18 which are approximately linear should be compared with the Tuck velocity plots of Figures 4-1, 4-2 and 4-3. There is obviously a difference in the velocity values. The Smythe maxima are 1.78, 4.04 and 8.29 (micr/min) at 21°, 31° and 41° respectively, whereas the approximate Tuck values at the same concentrations are 3.18, 5.28 and 8.59 (micr/min) at 20°, 30° and 40° respectively. The greatest difference is in the 21° maximum compared with the Tuck 20° value, whereas the 41° Smythe maximum is close to the Tuck value at 40°. Crystal growth increases with temperature, and it appears that readings taken over one hour are more adequate with higher temperatures (40° and over) with the exception of the very low supersaturation region (i.e. below $S = 1.06$).

It is significant that in this case the difference in crystallization velocity values does not depend upon the speed of the stirrer. The Smythe experiments were carried out at impeller speeds of 3,000 r.p.m. On the other hand, most of the Tuck experiments were effected at about 840 r.p.m. or less, depending on the viscosity of the solution.

However, it may well be the case that the Kucharenko results which are significantly lower than those of Smythe, were lower because there was so little stirring (1.2-1 r.p.m.). Smythe¹ in his earlier article on crystallization velocities maintained that the higher values secured by Vernon as compared with those of Kucharenko were due to conditions of high

relative velocity of crystal and syrup as against very low relative velocity of crystal and syrup.

Figures 4-19 and 4-20 illustrate the relationship between log crystallization velocity and log (S - 1) for the Smythe data, with S being calculated to both Kelly and Tuck solubilities. It was necessary to reduce the large number of observations in both the 21° and 41° sets of results, and the best 12 were chosen in each set. The observations omitted are marked x in Table 4-6.

The following rate equations were calculated:-

(a) With Kelly solubility:

$$k = 2.795 \times 10^{12} (S - 1)^{0.97} e^{-15,888/RT} \quad (4-12)$$

(b) With Tuck solubility:

$$k = 3.239 \times 10^{11} (S - 1)^{1.2} e^{-14,440/RT} \quad (4-13)$$

As with the previous results of Tuck and Kucharenko, the rate equation calculated to Tuck solubility was tested for degree of fit. The standard deviations were 6.81%, 5.45% and 6.64% at 21°, 31° and 41° respectively. The standard deviation over the three temperatures was 6.41%.

5. SOLUBILITY.

It has already been mentioned that there are considerable differences in the various solubility figures, and it would appear that the solubility figures at 20°, 30° and 40° determined in the current studies have done little to clarify the situation.

Table 4-7 sets out the solubility equations of the various workers in this field together with the quadratic formed from the solubilities at 20°, 30° and 40° in the current studies.

Figure 4-19. LOG CRYSTALLIZATION VELOCITY
V. LOG (S - 1)
 (SMYTHE)
 (S calculated to Kelly solubility)

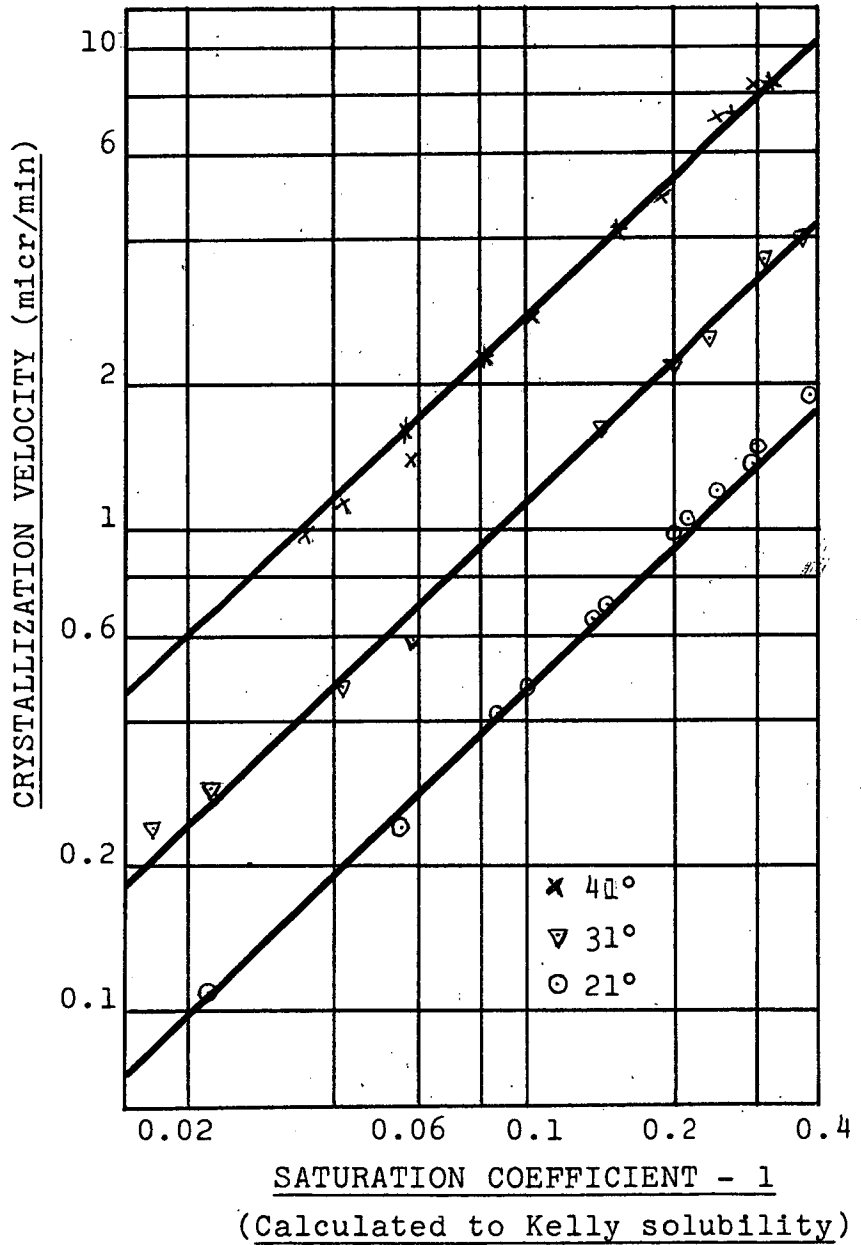


Figure 4-20. LOG CRYSTALLIZATION VELOCITY
V. LOG (S - 1)
 (SMYTHE)
 (S calculated to Tuck solubility)

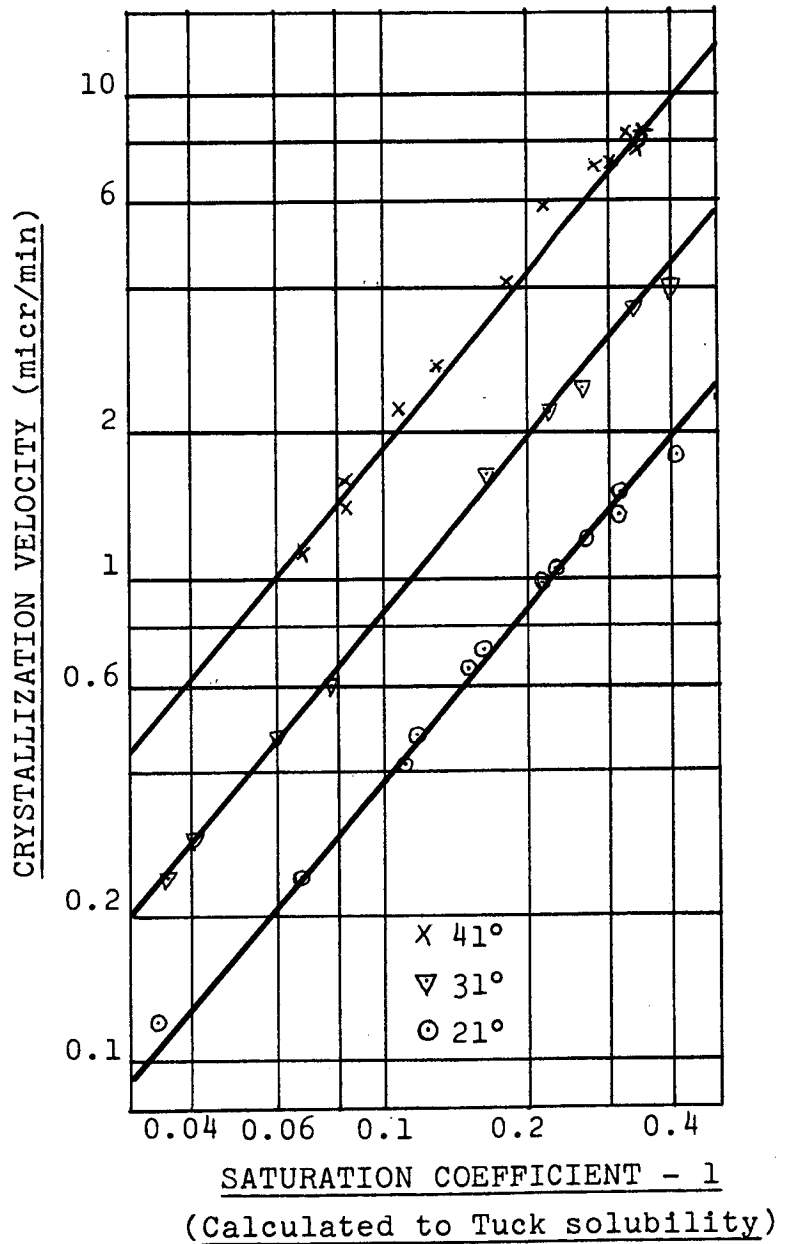


Table 4-7. SOLUBILITY EQUATIONS.

(1) Kelly ⁵ : $c = 64.53 + 0.0937t + 0.0012t^2$	$t < 46^\circ$	(4-14)
$c = 61.15 + 0.2249t - 0.0001t^2$	$t > 46^\circ$	(4-15)
(2) Vernon ⁶ : $c = 63.256 + 0.1497t + 0.000578t^2$		(4-16)
(3) Charles ⁷ : $c = 64.397 + 0.07251t + 0.0020569t^2$		
$- 9.035 \times 10^{-6}t^3$		(4-17)
(4) Vavrinecz ⁸ : $c = 64.447 + 0.08222t + 0.0016169t^2$		
$- 1.558 \times 10^{-6}t^3 - 4.63 \times 10^{-8}t^4$		(4-18)
(5) Tuck: $c = 64.54 + 0.081t + 0.0012t^2$		(4-19)

The Herzfeld solubility figures, accepted for so many years, have been discarded. Charles⁷ states that Herzfeld secured no solubility measurements between 60° and near 100° in his six observations from 5° to 100°, and that of his five lowest points only the one around 19° was approached from supersaturation. Moreover, Charles maintains that several days are required to reach equilibrium whereas Herzfeld's work was finished in a matter of hours.

Table 4-8 summarises the various solubility data. For comparison the Tuck values (10°-50°) are included. It is notable that apart from the 10° value (which is extrapolated from the equation) and the 20° value, these are lower than all of the other figures.

Why are there these differences in the solubility figures? The Tuck solubility is 5.6 g / 100 g water below the Kelly figure at 40°. It poses the question as to whether saturation is rather a region than an actual point at any temperature. Crystallization studies would appear to support this. For example, at 20° with $s = 1.9901$ the crystal began to grow after dissolving for 30 minutes. At 20° with $s = 1.9782$ the crystal

grew for 45 minutes. At 30° with $s = 2.1222$ the crystal grew for 30 minutes before dissolving for 15 minutes.

Table 4-8. SOLUBILITY DATA (g / 100 g water).

<u>t°</u>	<u>Kelly</u>	<u>Vernon</u>	<u>Charles</u>	<u>Vavrinecz</u>	<u>Tuck</u>
0	181.9	172.2	180.9	181.3	
10	190.6	184.2	188.4	188.4	189.5
20	201.9	198.3	199.4	200.3	199.8
30	216.7	215.2	214.3	215.5	213.0
40	235.6	235.2	233.4	235.4	230.0
50	259.6	259.5	257.6	259.5	256.4
60	288.8	289.8	287.6	288.7	
70	323.7	326.9	324.7	324.5	
80	365.1	374.7	370.3	370.8	
90	414.9	437.9	426.2	426.3	
100	476.0	525.5	494.6	477.4	

6. CRYSTALLIZATION ENERGY.

A computer programme was designed to calculate crystallization energy from the solubility data. This involved the application of the Clapeyron-Clausius equation to the solubility - temperature relationships in the following form,

$$\ln c_1/c_2 = \Delta H/R (T_1 - T_2)/T_1 T_2 \quad (1-19)$$

The results are given in Table 4-9. The values are very low compared with those secured in chapter 3, viz. 12,998 (20°), 13,410 (30°) and 13,801 (40°).

The equation of Lyle for the heat effect on dissolving sucrose in a solution of concentration s_1 to form a solution of concentration s_2 (1-18) may be arranged in the following way,

$$Qs_1 s_2 t = 850.2/(9+s_1)(9+s_2) - 11.1111 \\ - 0.126t - 0.00475t^2 \quad \text{cal/g sucrose} \quad (4-20)$$

Table 4-9. CRYSTALLIZATION ENERGIES FROM SOLUBILITY DATA.

<u>Name</u>	<u>Log Frequency Factor</u>	<u>Energy cal/g mol</u>	<u>Standard Deviation</u>
Kelly	5.818	2,025	1.23%
Vernon	5.037	2,271	1.44%
Charles	5.515	2,121	1.40%
Vavrinecz	5.653	2,077	1.27%

Table 4-10 sets out the crystallization energies obtained by means of the Lyle equation (4-20), using the Kelly solubilities at each temperature.

Table 4-10. CRYSTALLIZATION ENERGIES FROM THE LYLE EQUATION.

<u>Temp. °</u>	<u>Energy cal/g</u>	<u>Energy cal/g mol</u>
0	3.8454	1,316
10	5.6592	1,924
20	8.2479	2,823
30	12.2379	4,189
40	17.0059	5,821
50	22.7798	7,797
60	29.5349	10,110
70	37.2733	12,758
80	45.9880	15,742
90	55.6821	19,060
100	66.3594	22,714
Geometric Mean = 6,687		

Summary:

Thus we have data for crystallization energies derived from these independent sources of information, viz.,

- (a) From temperature coefficient of crystallization constant data;
- (b) From temperature coefficient of solubility data; and
- (c) From direct calorimetric observations.

It is of interest to note that the values obtained by direct observation are, at least at lower temperatures, closer to those calculated from solubility data than from those calculated from kinetic data. It is, however, thought pertinent to observe that the latter values are perhaps closer to those obtained for viscosity energy values. Whether this necessarily implies viscosity control of crystal growth or not is considered to be relevant to the problem, but not proved by direct test. It is thought that rather more sophisticated direct testing in relation to Reynold's number values is called for in order to be able to make worthwhile deductions on this matter.

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CONCLUSION

It has been shown that the viscosity of the sucrose - ethanol - water system decreases with the increase of ethanol concentration in the solvent. In the case of viscosity at saturation, the minima ranged from 80.2 cP at 82.5° with aqueous sucrose solutions to 15.40 cP at 30.5° with solutions having 0.5 mass fraction of water in the solvent.

Viscosity energies were calculated after determining the rate of change of viscosity of a particular solution with temperature. These values decreased as the proportion of alcohol in the solvent increased. The overall range covered was from 13.5 to 8.25 k.cal.

Rates of crystallization ($\text{mg}/\text{m}^2/\text{min}$) at three different temperatures were determined for the sucrose - ethanol - water solutions. Crystallization energies were calculated by means of the rate of change of the crystallization constant of a solution with temperature. These values decreased with the increase of ethanol in the solvent, and the overall range was 13.8 to 8.55 k.cal. Even granting that there is an approximation about the crystallization energy values, the similarity with the viscosity energy values suggests that viscosity is of substantial importance in sucrose crystallizing systems.

The study of crystallization and dissolution with aqueous sucrose solutions at 20°, 30° and 40° yielded some interesting data from which the following deductions were made:-

(1) The proposed first-order reaction,

$$k = n (c - c_s) \quad (3-3)$$

has been shown to lack validity at very low supersaturations, for $n \rightarrow \infty$ as $S \rightarrow 1.0$. In fact, the n v. S plot is only approximately linear in the region excluding very low supersaturations. It is concluded that the definition of the

crystallization and solution constants according to this equation is rather artificial, and hence the use of such concepts is limited. It is therefore believed to be best to concentrate studies in this field on the crystallization and solution velocities.

(2) New values for solubilities were secured as follows:- 1.998, 2.130 and 2.300 (g/g) at 20°, 30° and 40° respectively. It is notable that the 30° and 40° values are lower than those of other workers.

(3) Crystallization velocity values were higher than those of other workers, especially at low supersaturations. It has been suggested that this may be due to the shorter observation period, viz., three fifteen minute periods of observation, rather than a single observation at the end of an hour.

It is interesting to set down together the various rate equations calculated with the Tuck solubility data:-

$$(a) \text{ Tuck: } k = 6.498 \times 10^7 (S - 1)^{0.485} e^{-9,555/RT} \quad (4-6)$$

$$(b) \text{ Kucharenko: } k = 2.419 \times 10^7 (S - 1)^{1.6} e^{-9,658/RT} \quad (4-11)$$

$$(c) \text{ Smythe: } k = 3.239 \times 10^{11} (S - 1)^{1.2} e^{-14,440/RT} \quad (4-13)$$

The energy terms of the Tuck and Kucharenko rate equations are very close to each other, whereas that of the Smythe rate equation is about 50% higher than the Kucharenko value.

(4) It is considered that the solution studies should prove to be of significance, since there is an almost complete lack of detailed research in this field. The rate equation calculated with Tuck solubility data was,

$$k = - 2.393 \times 10^9 (1 - S)^{1.26} e^{-9,906/RT} \quad (4-9)$$

(5) Arising from these studies is the observation of substantial differences in values calculated for heat of

crystallization from varying conditions of observation, and the need for reconciliation with the directly observed values.

It is considered that further studies of the place of viscosity in the mechanism of crystallization are still required for clarification.

APPENDIX. EXAMPLES OF CALCULATIONS.

1. MINIMUM VISCOSITY AT SATURATION of solutions with mass fraction of water 0.7 (chapter 2):

$$\mu = a + bT + cT^2$$

$$71.00 = a + 293.16b + 293.16^2c \quad (1)$$

$$52.53 = a + 303.16b + 303.16^2c \quad (2)$$

$$51.89 = a + 313.16b + 313.16^2c \quad (3)$$

$$(2) - (1) - 18.47 = 10b + 5963.2c$$

$$(3) - (2) - \underline{0.64} = 10b + 6163.2c$$

$$17.83 = 200.0c; \quad c = \underline{0.08915}.$$

$$10b = -18.47 - 531.62 = -550.09; \quad b = -\underline{55.009}$$

$$a = 71.00 + 16126.4 - 7661.8 = \underline{8,535.6}$$

$$\text{Minimum Temp.} = -b/2c = 55.009/0.1783 = 308.52^\circ \text{K} = \underline{35.36^\circ \text{C.}}$$

$$\text{Minimum } \mu = 8535.6 - 16971.3 + 8485.7 = \underline{50.0 \text{ cP.}}$$

2. VISCOSITY ENERGY of solution with mass fraction of water 1.0; saturation temperature 20°; 66.89% sucrose (chapter 2).

$$RT \ln \mu = A + BT \quad (2-4)$$

$$3147.8 = A + 293.16B$$

$$\underline{2537.0} = A + 313.41B$$

$$-610.8 = 20.25B;$$

$$B = -\underline{30.163}; \quad e^B = 7.9416 \times 10^{-14}$$

$$\text{Hence } A = 3147.8 + 8842.6 = 11,990.4$$

$$t = 30.2^\circ: A = 2800.7 + 9150.3 = 11,951.0$$

$$\text{Average } A = \underline{11,971}.$$

3. CRYSTALLIZATION ENERGY of a solution with mass fraction of water 0.9; saturation temperature 20°; 63.24% sucrose (chapter 3):

$$RT \ln n = A + BT \quad (3-4)$$

$$2224.1 = A + 283.16B$$

$$\underline{2370.7 = A + 286.16B}$$

$$146.6 = 3.00B; \quad B = \underline{48.867}$$

$$A = 2224 - 13837 = - \underline{11,613}$$

(The 16° value is ignored in the calculation of A.
See pages 3-8 and 3-13)

$$16^\circ: \quad TR \ln n_{\text{obs}} = 289.16 \times 9.3333$$

$$TR \ln n_{\text{calc}} = -11613 + 14130 = 2,517$$

$$R \ln n_{\text{calc}} = 8.7045$$

$$\text{St.D. } (R \ln n) = \pm \sqrt{0.62882/3} = \pm \sqrt{0.13179} = \pm 0.3631$$

$$\text{St.D. (as \% of calc. value)} = \pm 36.31/8.7045 = \pm \underline{4.17\%}.$$

4. CRYSTALLIZATION VELOCITY in aqueous sucrose solution, concentration 4.0679 g/g, at 20° (chapter 4):

$$k = (1063.45 \times p_2^{1/3} - 1063.45 \times p_1^{1/3}) / \theta \quad (4-1 \text{ and } 4-2)$$

$$= (1063.45 \times 506.904^{1/3} - 1063.45 \times 497.062^{1/3}) / 10$$

$$= (8479.3 - 8424.0) / 10$$

$$= \underline{5.53} \text{ microns / minute}$$

5. RATE EQUATION: Tuck Crystallization Velocity Equation using Tuck Solubility (chapter 4):

$$\log k = a \log (S-1) + b \quad (4-4)$$

The calculation uses the plot (Figure 4-11)

$$40^\circ: k = 1; \quad (S-1) = 0.0042 = 1/238.2$$

$$k = 10; \quad (S-1) = 0.484 = 1/2.065$$

$$\text{Equation (4-4):- } 0 = -2.3770a + b$$

$$\underline{1.0 = -0.3151a + b}$$

$$1.0, = 2.0619a;$$

$$a = 0.485; \quad b = 1.1529$$

$$k = 14.22 (S-1)^{0.485}$$

$$20^\circ: k = 1; \quad (S-1) = 0.037 = 1/27.03$$

$$k = 4; \quad (S-1) = 0.645 = 1/1.55$$

$$\text{Equation (4-4):- } 0 = -1.4318a + b$$

$$\underline{0.6021 = -0.1903a + b}$$

$$0.6021 = 1.2415a;$$

$$a = 0.485; \quad b = 0.6944$$

$$k = 4.948 (S-1)^{0.485}$$

$$1.1529 = z + 0.000697Q$$

$$\underline{0.6944 = z + 0.000745Q}$$

$$0.4585 = -0.000048Q; \quad Q = -9,555.$$

$$z = 1.1529 + 6.6598 = 7.8127$$

$$\underline{k = 6.498 \times 10^7 (S-1)^{0.485} e^{-9,555/RT}}$$

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NOMENCLATURE

- c = the concentration (g sucrose / 100 g water unless specified)
- c_s = the concentration at saturation
- cP = centipoises
- C = a constant
- d = the diameter
- ° = ° Centigrade
- g = grams
- k = the velocity of crystallization or solution
- M = the mass
- μ = the viscosity
- n = the crystallization or solution constant
- N = the Avogadro number (6.02×10^{23} / mole)
- p = the crystal weight in mg (unless specified)
- Δp = the increase in crystal weight in mg
- r = the radius
- R = the gas constant (1.987 cal. / degree / mole)
- ρ = the density
- s = the concentration (g sucrose / g water)
- S = the supersaturation or saturation coefficient
- St.D. = the standard deviation
- σ = the surface area (of crystal or crystals)
- t = ° Centigrade
- T = ° K (Kelvin or absolute) = $273.16 + ^\circ\text{C}$.
- θ = the time in minutes (unless specified)
- v = the volume

Kucharenko formula (1-1):

- p = the crystal weight in g

Noyes and Whitney equations and modifications (1-2,.... 1-7)

- c_1 = the concentration at time θ_1
- c_2 = the concentration at time θ_2
- K_M = the coefficient of mass transfer

NOMENCLATURE

Noyes and Whitney equations and modifications (cont'd):

- M = the mass deposited in time θ
- D = the coefficient of diffusion of the solute
- x = the length of diffusion on the path
- K_D = the coefficient of mass transfer by diffusion
- c_i = the solute concentration in solution at the interface
- K_r = the rate coefficient for the surface reaction

Film and Surface Renewal Theories; Mass Transfer Rate (1-8, 1-14):

- x = equivalent film thickness
- f = the fractional rate of surface renewal
- D = the diffusivity of solute molecules in the liquid

Velocity of Condensation equations (1-9, 1-10):

- r^* = the radius of the critical nucleus
- ψ = the vapour pressure
- M = the mass of a molecule
- τ = the liquid-gas interfacial tension
- v_l = the chemical potential per molecule in the liquid phase
- v_g = the chemical potential per molecule in the gas phase
- m^* = the maximum number of molecules, corresponding to the critical nucleus

Becker Nucleation Rate (1-11):

- v = the activation energy of diffusion
- A(T) = the work necessary to produce the nucleus surface

Crystallization Velocity equations (1-12, 1-13):

- v = the molar volume
- λ = the latent heat of transition
- V = the crystallization velocity

Reaction Rate and Stirring (1-16):

- I = the rate of stirring
- α = a constant
- β = a constant

NOMENCLATURE

Kaganov and Zhigalov (Kucharenko) Crystallization Rate (1-17):
 ΔS_u = the surplus sucrose concentration expressed as molality

Clapeyron-Clausius equation (1-19):

c_1 = the concentration of a saturated solution expressed as a molefraction at temperature T_1

c_2 = the concentration of a saturated solution expressed as a molefraction at temperature T_2

ΔH = the heat of crystallization

Heat equation (1:20):

Q = the heat of crystallization

α = a characteristic constant of the system

β = a characteristic constant of the system

Viscosity equation (2-1):

μ = the viscosity in centipoises

θ = the period of fall of the ball in seconds

ρ_b = the density of the ball

ρ_l = the density of the liquid at the measuring temperature

C_b = the ball constant

Arrhenius and modified Arrhenius equations (2-2, 2-3 and 2-4):

A = a characteristic constant in the Arrhenius equation

B = a characteristic constant in the Arrhenius equation

ϕ = a characteristic constant in the modified Arrhenius equation

Standard Deviation formula:

y_{obs} = the value for the condition studied

y_{calc} = the calculated value

m = the number of observations

* $P = a$ characteristic constant in the Arrhenius equation
 $= e^{B/R}$

NOMENCLATURE

Polynomials (Tables 2-5, 3-6 and 4-7):

Su = the percentage of sucrose

c = the solubility of sucrose as a percentage

W = the mass fraction of water

Crystallization Energy equations (3-5, 3-6):

A = a characteristic constant of the system

B = a characteristic constant of the system

Velocities of Crystallization and Solution (4-3, 4-4 and 4-7):

z = a characteristic constant of the system

m = a characteristic constant of the system

Q = a characteristic constant of the system

a = a constant

b = a constant