THE CRYSTAL HABITS OF COINAGE METALS GROWN BY REVERSIBLE OXIDATION REDUCTION REACTIONS IN AQUEOUS SOLUTIONS

by

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INTRODUCTION

It is obvious that the preparation of many metals by reduction from their compounds has been known for centuries. It is equally well known that metals are oxidized by various solutions. The reaction whereby a metal is oxidized by a hot solution and then the resulting solution is reduced back to the metallic state on cooling is a more recent discovery. Berzelius (4), for example, noted that metallic copper was attacked by a hot solution containing cupric ion and that powdered copper precipitated from this solution when it was cooled.

If this reaction is carried out in a dynamic way the result is a mass transfer from hot to cold sections of the apparatus. Mass transfer phenomena have been reported for a number of systems. Metallic iron has been reported to be transferred by liquid sodium (12) and liquid lithium (59). Liquid lead will transfer beryllium, iron, chromium, cobalt, titanium and nickel (20). Molten sodium hydroxide will transfer nickel (53). In other cases solutions bring about the mass transfer. Solutions of cupric sulphate will transfer copper and solutions of ferric ion will transfer silver.

Many of these transfers are the results of solubility changes due to temperature changes while others are due to reversible oxidation - reduction reactions. Some of the reactions, such as the one with copper mentioned above, occur by means of an intermediate unstable oxidation state which becomes more stable at high temperatures but disproportionates on cooling. The reaction in this case is

$$Cu^{++} + Cu \rightleftharpoons 2\ Cu^{+}$$

In other cases there seems to be no evidence for the existence of such unstable oxidation states, as for example in the reaction

$$Fe^{++} + Ag^{+} \rightleftharpoons Fe^{+++} + Ag$$

In spite of the fact that many of these reactions have been known for some time very little attention seems to have been paid to the physical characteristics, in particular the crystal habits, of the metal powders produced.

That solid materials can change their crystal habits under certain conditions has also been known for quite some time. These habit modifications have been noted mainly in the crystallization of solids from solution. Although these habit modifications are known, very few reports on them have appeared in the literature. A change of solvent or the presence of some foreign substance in the solution are the factors causing this change which have been chiefly investigated. As yet there seems to be no adequate theory to explain these modifications in spite of many attempts to devise one. These are dealt with more fully in the section on crystal growth below.

Many studies have been made on the growth of crystals in an effort to gather information for the development of a theory of the mechanism of the nucleation and growth of crystals. These studies have been restricted mainly to the following types of systems:

(a) crystal growth by deposition from the vapour state,
(b) crystal growth from the liquid state i.e., freezing,
(c) crystal growth by evaporation of saturated solutions,
(d) crystal growth by cooling of hot solutions,
(e) crystal growth by the formation of an insoluble substance as a result of a chemical reaction in solution.

In this last group studies have dealt primarily with the conditions for obtaining precipitates which are free from contaminants and with good filtering characteristics for purposes of quantitative analysis. Few studies in this group have been made from the point of view of crystal habit. As far as metals are concerned, the study by Courtney (22) on the precipitation of silver from solution by reduction with ferrous ion seems to be the only one which has been made. This study dealt mainly with the kinetics of whisker growth rather than with crystal habit modifications. Kohlshutter and Steck (50) had noted that silver formed by this reaction appeared as triangular and hexagonal plates as well as in dendritic forms. In some preliminary work preceding this investigation it had been noted that the copper powder formed by the disproportionation of cuprous ion assumed a variety of habits.

In view of the remarks above it was decided to undertake an investigation of the factors which affected or governed the crystal habits assumed by the copper powder. In time the investigation was extended to the formation of crystalline silver and gold so that the investigation eventually covered the coinage metals.

THE CHEMICAL REACTIONS

Copper. Berzelius (4) was apparently one of the first investigators to notice that cupric sulphate solutions attacked copper metal and he speculated about the existence of cuprous sulphate. Other workers attempted to use this reaction as a method for the preparation of cuprous sulphate without success. Kiliani (49) investigated the sludge formed at the anode during the electrolysis of cupric sulphate solutions between copper electrodes and he showed that cuprous sulphate had been formed by its decomposition into metallic copper.

Hiller (43) and Mallett (58) reported the formation of crystalline copper when copper sheets were placed in a solution of cupric nitrate. Forster and Seidel (33) found that using cupric sulphate in place of the nitrate decreased the rate of reaction but that an increase in temperature caused an increased amount of attack on the metal. They reported the reaction to be reversible as copper deposited out on cooling.

Recoura (81) prepared cuprous sulphate as a grey powder by the reaction of cuprous oxide with dimethyl sulphate. It was found to be stable in dry air but to react with water

$$Cu_2SO_4 + H_2O \longrightarrow CuSO_4(aq) + Cu + 21 \text{ cals.}$$

Recoura explained the instability of the cuprous sulphate in the presence of moisture to be a result of the exothermic reaction.

Abel (1) made one of the earliest determinations of the equilibrium constant for the disproportionation of the cuprous ion. An acid cupric sulphate solution was kept in contact with rods of copper at 100°C. The cuprous ion content of the solution was determined by the loss in weight of the copper rods. The solution was rapidly cooled to 25°C and the copper which precipitated out was weighed. These data were used to calculate the equilibrium constant at 25°C on the assumption that the cuprous salt was completely dissociated and that the cupric sulphate was 17% dissociated. The value reported for the ratio $(Cu^+)^2/(Cu^{++})$ was 0.66×10^{-8}. The result is low compared with later work and Heinerth (42) claimed that the method was highly inaccurate.

Luther (56), (57) placed copper rods in an acid solution of cupric sulphate in sealed tubes and allowed the system to come to equilibrium in a thermostated bath. The contents of the tube were quickly filtered, on opening, and titrated potentiometrically with permanganate. The value of the ratio $(Cu^{++})/(Cu^+)^2$ was reported as 1.5×10^6. The result is probably in error as some of the cuprous salt would be oxidized by atmospheric oxygen during the manipulations. Luther made the same assumptions as Abel about the degree of dissociation of the salts.

Fenwick (32) determined the equilibrium constant using a similar technique as Luther but the titrations were carried out in an inert atmosphere. Using sulphate and perchlorate solutions the value of the ratio $(Cu^{++})/(Cu^+)^2$ at 25°C was found to be 1×10^6. She also determined the standard potentials of the various copper systems and proved that the cuprous ion was monovalent.

Heinerth (42) redetermined the value of the equilibrium constant working in an inert atmosphere and titrating the solutions with ceric sulphate. Determinations were made at various temperatures using sulphate and perchlorate solutions. His results for sulphate solutions are listed in Table I.

Table I.

Equilibrium constant for the cupric - cuprous system.

Temp. °C	$\sqrt{(Cu^{++})}/(Cu^{+})$	
101	40	(approximation only)
60	205	
50	319	
40	500	
30	835	
20	1429	

The value of the ratio $\sqrt{(Cu^{++})}/(Cu^{+})$ at 25°C was determined graphically as 1091 which agrees well with the value of 1100 obtained by calculation from Fenwick's data. The value appeared to be independent of the ionic strength of the solution.

The value of this ratio for perchlorate solutions at 25°C was 956 and Fenwick reported a value of 1300. Heinerth attributed the difference to the presence of chlorides in the solutions used by Fenwick and stated that the presence of these would slow the attainment of equilibrium during titration.

Heinerth also determined the heat of the reaction

$$\frac{1}{2}\,Cu^{++} + \frac{1}{2}\,Cu \rightleftharpoons Cu^{+}$$

graphically using his data and the van't Hoff isochore. The heat of reaction was - 9410 calories per mol of cuprous ion with sulphate solutions and - 9390 with perchlorate solutions.

A solution of sulphuric acid will attack metallic copper and cupric sulphate is one of the products formed. This forms a solution of cupric sulphate which in turn attacks the metallic copper. Hence, solutions of sulphuric acid can eventually have the same effect on metallic copper as solutions of cupric sulphate.

Gold. Gold is not attacked by sulphuric acid alone but the presence of oxidizing agents will allow the gold to be attacked (90). Solutions of sulphate salts do not appear to dissolve gold. Nitric acid attacks gold slightly. The resulting solution is unstable unless there is a substance present to stabilize the gold ions produced by forming complexes with them (66).

McIlhiney (64) and McCaughey (63) reported that HCl had no solvent effect on gold in the presence of air. Lenher (55) and Ogryzlo (75) reported that HCl dissolved gold at high temperatures and pressures. Krauskopf (52) calculated the equilibrium constant for the reaction

$$Au + 3\ H^+ + 4\ Cl^- \rightleftharpoons AuCl_4^- + \tfrac{3}{2}\ H_2$$

at 25°C to be 10^{-51} from the available thermodynamic data. No data are available for the calculation of the effects of temperature and pressure changes on the reaction.

In solution gold can exist in two oxidation states, the aurous or monovalent form and the auric or trivalent form. At room temperature the aurous salts are unstable and decompose

$$3\ Au^+ \rightleftharpoons Au^{+++} + 2\ Au\ .$$

The auric ion is a strong oxidizing agent and can exist in solution only as a complex ion, hence the above equilibrium cannot be investigated directly. In alkaline solution the AuO_2^- ion is the stable species. In acid solution the trivalent state is stable only in the presence of a strong complexing agent such as the chloride ion. The stable form is then the $AuCl_4^-$ ion.

The compound $Au(OH)_3$ is amphoteric and the following ionization constants are reported:

$$Au(OH)_3 \rightleftharpoons Au^{+++} + 3\ OH^- \qquad K = 8.5 \times 10^{-45} \qquad (46)$$

$$Au(OH)_3 \rightleftharpoons H^+ + H_2AuO_3^- \qquad K = 6 \times 10^{-18} \qquad (47)$$

$$H_2AuO_3^- \rightleftharpoons H^+ + HAuO_3^= \qquad K = 5 \times 10^{-14} \qquad (47)$$

$$HAuO_3^= \rightleftharpoons H^+ + AuO_3^{\equiv} \qquad K = 10^{-16} \qquad (47)$$

The complex ion $AuCl_4^-$ is reported by Bjerrum and Kirschner (5) to have an instability constant of 5×10^{-22}. An aqueous solution of auric chloride has been shown to be a solution of the acid $H[AuCl_3OH]$ by Kharasch and Isbell (48). Undoubtedly all stages of mixed complexes from $[Au(OH)_4]^-$ to $AuCl_4^-$ exist with this latter ion being the most stable.

Latimer (54) estimated the equilibrium constant for the reaction

$$3\ Au^+ \rightleftharpoons Au^{+++} + 2\ Au$$

to be about 10^{10}. It can be seen then, that a solution of a gold salt is a complicated mixture of various complexes. The addition of other ions such as the hydrogen ion and the chloride ion can have a widespread effect upon all these equilibria.

Wohlwill (100) found that gold was attacked by a hot solution of $AuCl_3$ and that crystalline gold separated on cooling. Hanriot and Raoult (41) reported the same results for solutions of auric chloride in hydrochloric acid and reported that the attack on the gold was proportional to the concentration of $AuCl_3$. Bose (7) and Morris (71) attributed the reaction to the formation of aurous chloride and the shifting of the equilibrium position of the reaction with changes in temperature.

Stokes (88) dissolved gold in hot solutions of ferric chloride in hydrochloric acid. Brokaw (10) claimed that this solution had no effect. McIlhiney (64) reported no effect unless oxygen was present. McCaughey (63) showed that doubling the acid concentration increased the attack on the gold by a factor of 1.5 and doubling the salt concentration increased the attack by a factor of 1.4. The action of the ferric ion seemed to vary inversely with the concentration of ferrous ion. Krauskopf (52) calculated the equilibrium constant for the reaction

$$3\ Fe^{+++} + Au + 4\ Cl^{-} \rightleftharpoons AuCl_4^{-} + 3\ Fe^{++}$$

to be about 10^{-12} at 25°C. This indicates that a high concentration of ferric ion is required to attack the gold and that ferrous ion would decrease the solubility. The reaction would also be highly sensitive to chloride ion concentration.

Brokaw (10) dissolved gold in a solution of ferric chloride and manganese dioxide in hydrochloric acid. The reaction was attributed to the action of free chlorine on the gold. Krauskopf (52) gives a value of 10^{28} for the equilibrium constant for the reaction

$$2\ Au + 12\ H^{+} + 3\ MnO_2 + 8\ Cl^{-} \rightleftharpoons 3\ Mn^{++} + 2\ AuCl_4^{-} + 6\ H_2O.$$

The reaction is very sensitive to the pH and chloride ion concentration of the solution.

Wurtz (102) claimed that gold would dissolve in a solution of ferric sulphate. Stokes (88) found that a solution of ferric sulphate in sulphuric acid was inactive unless chloride ion was present. Brokaw (10) reported solutions of ferric sulphate in sulphuric acid to have no effect even upon the addition of manganese dioxide. Milner (69) reported that gold was unattacked by a cold solution of ferric sulphate in sulphuric acid but on standing overnight the solution gave a test for gold. A hot solution gave a test after fifteen minutes. A boiling solution dissolved gold foil and, on cooling, this solution precipitated feathery crystals of gold. Krauskopf (52) states that it is impossible for gold to dissolve in a solution of ferric sulphate in sulphuric acid since there is nothing present to complex the auric ion and stabilize it. For the reaction

$$2\ Au + 8\ Cl^- + 12\ H^+ + 3\ SO_4^{=} \rightleftharpoons 2\ AuCl_4^- + 3\ H_2SO_3 + 3\ H_2O$$

at 25°C he calculated the equilibrium constant to have a value of 10^{-81}.

Silver. Unlike copper and gold, silver does not have a lower oxidation state which disproportionates to the metal and a higher oxidation state. In the case of silver the +1 oxidation state is stable. If silver crystals are to be formed from massive silver a reversible oxidation-reduction reaction involving metallic elements other than silver must be used.

Sulphuric and nitric acids will attack silver under the proper conditions but the reactions are not reversible. Jellinek (45) reported that silver dissolved at 80° - 100°C in the presence of silver ion in a circulating system. This was taken as evidence for the reaction

$$Ag + Ag^+ \rightleftharpoons Ag_2^+.$$

Crystals were reported to form in the cold section of the apparatus. However, if all the reagents were carefully purified no reaction occurred. Jellinek concluded from this that some impurity must have been acting as a catalyst. It could be possible that the impurity itself attacked the silver and the presence of the silver ion was unnecessary.

Stokes (88) reported a reaction between metallic silver and hot cupric sulphate solutions.

$$2\ Ag + 2\ CuSO_4 \rightleftharpoons Cu_2SO_4 + Ag_2SO_4.$$

No metallic copper is formed from the disproportionation of the cuprous ion since this ion reacts with the silver ion in solution to reverse the reaction. Edgar and Cannon (30) reported free energies and equilibrium constants for the reaction at 25°C and 40°C. They carried out their experiments in the presence of sulphate ions so that complexes are probably involved in their results.

The reaction

$$Ag + Fe^{+++} \rightleftharpoons Fe^{++} + Ag^{+}$$

has been the subject of a number of investigations. Hils (44) investigated the action of ferrous salts on metallic silver. Gmelin (36) reported that silver was attacked by a hot solution of ferric sulphate and that metallic silver separated out on cooling. Pisharewsky (79) reported a value of 0.00793 for the equilibrium constant at 25°C using sulphates. Tananaeff (91) reported a value of 0.0018 at 0°C, 0.0061 at 25°C and 0.0110 at 45°C. Dover (29) reported a value of 0.0070 at 25°C. Noyes and Brann (74) reported a value of 0.128 at 25°C using nitrates. Schumb and Sweetser (84) determined a value of 0.531 at 25°C using perchlorates. They recalculated the results of Noyes and Brann, taking into account the extent of the hydrolysis of the ferric ion and obtained a value of 0.363.

Roberts and Soper (82) found that an induction period of fifteen to twenty minutes was necessary before any metallic silver appeared when ferrous sulphate and silver nitrate were mixed at 25°C. This induction period was decreased by the presence of colloidal silver particles. An increase in hydrogen ion concentration increased the reaction rate. They concluded that the induction period was due to the time required for nucleation of silver crystals. They explained the effect of hydrogen ion as an influence on the speed of deposition of silver atoms on the nuclei and did not attribute the effect to a reaction with the reagent ions.

CRYSTAL GROWTH

It is convenient to divide the process of crystal growth into two steps: a nucleation step in which submicroscopic particles are formed and the growth of these nuclei into fully developed crystals. The first step is difficult to observe experimentally but there appears to be general agreement about the following observations on nucleation: (31)

(a) On cooling a solution a metastable region of supersatuuation occurs.

(b) The extent of this region of metastability can be changed by the presence of dissolved foreign substances.

(c) The rate of nucleation increases with the degree of supercooling, i.e., with the extent of the metastable region.

(d) The presence of solid foreign bodies (e.g. dust, etc.) and agitation can induce nucleation.

Observations on the growth of nuclei into crystals appear to be contradictory. Egli and Zerfoss (31) reported that the growth rate of a crystal increases with increasing supersaturation while Bunn and Emmett (17) claimed to have found no relation between the growth of a crystal face and supersaturation.

Gibbs (35) suggested an analogy between the growth of liquid drops and the growth of crystals. An isolated liquid drop is stable if its surface free energy, and hence its area, is a minimum. A crystal at constant temperature and pressure, in equilibrium with its surroundings should have a minimum Gibbs free energy for a given volume. If the volume free energy per unit volume is constant then

$$\sum_{1}^{n} \sigma_i A_i = \text{minimum} \qquad (1)$$

where σ_i is the surface free energy per unit area of face i and A_i is the area of this face on a crystal which has n faces.

The growth of a perfect crystal must occur by nucleation of a single layer "island" on a perfect crystal face and then by the extension of this "island" to the surface edges. Gibbs suggested that the nucleation of a new growth layer would occur at large supersaturations and that there would be a minimum or critical supersaturation for the nucleation of this new layer to occur.

The ideas of Gibbs have been extended by others. Curie (24) calculated the shapes of crystals in equilibrium with solutions which would result from a free energy minimum for a given volume. Wulff (101) deduced a relationship between the equilibrium shape of a crystal and the relative surface free energies of the faces.

Suppose p_i is the perpendicular from a point P within the crystal to the ith face of the crystal which has an area A_i. The volume of the crystal, V, is the sum of the volumes of the pyramids with P as a vertex and the crystal faces as bases.

$$V = \frac{1}{3} \sum_{1}^{n} p_i A_i \; . \tag{2}$$

The total free energy, F, is given by equation (1) as

$$F = \sum_{1}^{n} \sigma_i A_i \; .$$

If one set of faces grows by the disappearance of another set then

$$dV = \sum_{1}^{n} A_i \, dp_i \tag{3}$$

and from equation (2)

$$dV = \frac{1}{3} \sum_{1}^{n} (A_i \, dp_i + p_i \, dA_i) \; . \tag{4}$$

At constant volume, (the restriction imposed by Gibbs) $dV = 0$ whence

$$\sum_{1}^{n} p_i \, dA_i = 0 \quad . \tag{5}$$

At constant free energy and assuming σ is independent of A

$$\sum_{1}^{n} \sigma_i \, dA_i = 0 \quad , \tag{6}$$

From equations (5) and (6) for faces on which it is possible to vary A_i independently

$$p_i \propto \sigma_i \quad . \tag{7}$$

The crystal should form an equilibrium shape such that the perpendiculars from a point within the crystal are proportional to the specific surface free energies of the faces. This implies also that the rate of growth of a face in the direction normal to the face is proportional to the specific surface free energy. A more general proof of this theorem has been given by Herring (38).

The above deductions are limited by the fact that they are applied to the condition of a crystal in equilibrium with its surroundings. For most cases of crystal growth this condition is not met.

Various workers have extended the single layer nucleation aspect of Gibbs' theory of layer growth. It has been treated quantitatively by Kossel (51), Stranski (89), Becker and Doring (3) and Frenkel (34).

The free energy of formation of a single layer island consists of a volume contribution and a surface contribution. The volume contribution is negative for supersaturation conditions and the surface contribution is always positive. The volume contribution is proportional to the square of the "island" radius, assuming the "island" is circular. The surface contribution is proportional to the radius. From this it is seen that the surface contribution is important at small radii and the volume contribution is important at large radii. The free energy curve as a function of the island radius for a constant supersaturation will follow the course shown in Fig. 1. The maximum point represents a barrier which the island must overcome in order to become stable.

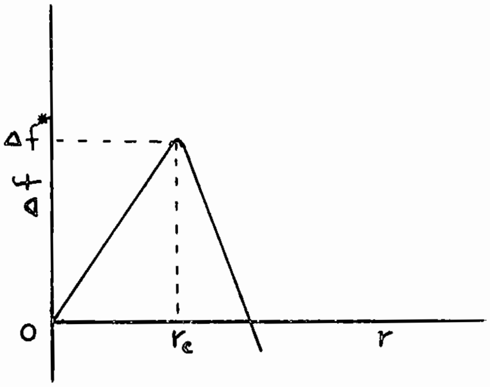


Fig. 1
Free Energy vs. Radius
After Sears (87).

Suppose an island has a radius r and that it is a single layer thick, then the free energy of formation Δf is given by

$$\Delta f = 2\pi r \sigma a + \pi r^2 a \Delta F_v \qquad (8)$$

where σ is the specific surface free energy, a is the interplanar distance and ΔF_v is the volume free energy for material deposition.

Since the free energy has a maximum, equation (8) can be differentiated with respect to the radius and equated to zero.

$$\frac{d\,(\Delta f)}{dr} = 2\pi a \sigma + 2\pi r a \Delta F_v = 0 \qquad (9)$$

This can be solved for r to give the value of the critical radius size r_c which must be attained if the island is to continue to grow.

$$r_c = -\frac{\sigma}{\Delta F_v} \qquad (10)$$

The value of Δf^*, the maximum value of Δf, then becomes

$$\Delta f^* = 2\pi a r_c \sigma + \pi r_c^2 a \Delta F_v$$

and substitution of equation (10) gives

$$\Delta f^* = -2\pi a \sigma . \frac{\sigma}{\Delta F_v} + \frac{\pi \sigma^2}{\Delta F_v^2} . a . \Delta F_v$$

$$= -\frac{\pi a \sigma^2}{\Delta F_v} . \tag{11}$$

According to the rate theory developed by Becker and Doring (3) and Volmer and Schultze (96) the number of nuclei formed per second on one square centimeter of surface by deposition from the vapour phase N, is given by

$$N = Be^{-\Delta f^*/kT}$$

where B is approximately 10^{20} $\sec^{-1}$, k is the Boltzmann constant and T the absolute temperature. Substitution of the expression obtained for Δf^* in equation (11) leads to

$$N = Be^{\pi a \sigma^2/kT \Delta F_v} . \tag{12}$$

ΔF_v can be expressed as a function of the supersaturation ratio α, where $\alpha = P/P_o$. P is the actual pressure of the depositing vapour and Po the vapour pressure. Then

$$\Delta F_v = -\frac{\rho RT}{M} \ln \alpha$$

in which ρ is the density of the condensed phase, R the gas constant and M the molecular weight of the material. Substitution of this into equation (12) yields

$$N = Be^{-\pi a \sigma^2 M/\rho kRT^2 \ln \alpha} . \tag{13}$$

Assuming that the behaviour of a solute in a solution is analogous to that of a vapour, equation (13) can be applied to the process of crystal growth from a solution. It applies to an atomically smooth crystal face.

The work of Volmer and Schultze (96) established that there was no critical supersaturation below which crystal growth did not occur.

Kossel (51) suggested a model of a crystal with a step on its surface (Fig. 2). The step on the crystal surface can have a "kink" on it as shown at point A. The kink can be considered as either positive or negative according to whether it advances from the step or recedes into it. Particles on the flat surface of the crystal face are attracted by five other particles, those on the edge of the step by four and those at a kink by three.

As the temperature of the crystal is increased the particles acquire energy and some are capable of leaving the surface. Other particles will be attracted to the surface. At a higher temperature the crystal surface will have the appearance shown in Fig. 3.

Burton, Cabrera and Frank (19) have shown that at equilibrium the number of positive kinks n_+ and the number of negative kinks n_- are equal and that

$$n_+ = n_- = e^{-w/kT}$$

where k is the Boltzmann constant, T the absolute temperature and w the energy required to form a kink. They estimate w to be about W/12 where W is the evaporation energy. They have also shown that the average distance between kinks, x, is given in terms of the interatomic distance a as

$$x = \frac{1}{2} a e^{w/kT} + 2 \approx \frac{1}{2} a e^{w/kT} .$$

Using ϕ as the nearest neighbour interaction and estimating ϕ to have a value of W/6

$$x = \frac{1}{2} a e^{\phi/2kT} .$$

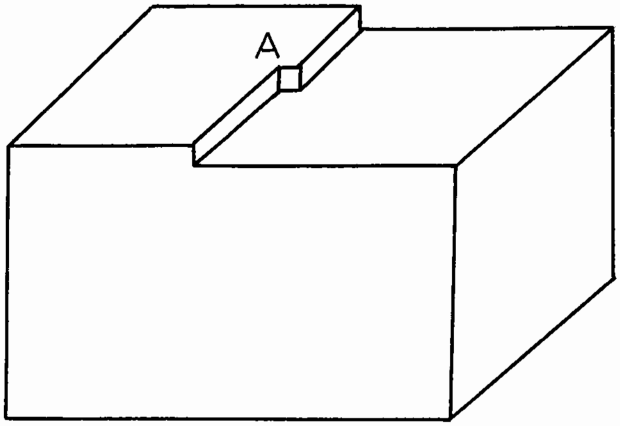


FIG. 2
Crystal surface at low temperature.

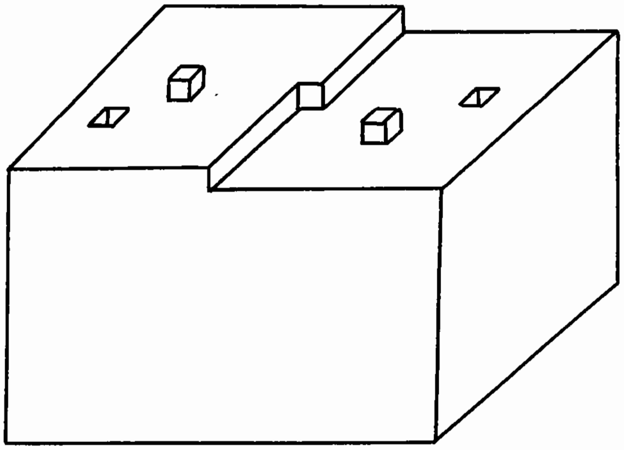


FIG. 3
Crystal surface at high temperature.

When the temperature T is between one half and four fifths of the boiling temperature in degrees absolute, ϕ/kT is about 4 and x is approximately 4a, i.e., there is a kink for every four molecules in the step. With this large number of kinks growth should occur more easily than with an atomically smooth face.

The work of Volmer (94) on the crystal growth of mercury showed that adsorbed molecules diffuse over the crystal surface towards a kink.

Burton, Cabrera and Frank (19) estimated the fraction of surface covered by adsorbed molecules, n_s, as

$$n_s = e^{-W_s/kT}$$

where W_s is the energy of evaporation from the kinks onto the surface and this was estimated to be $\frac{1}{2}$ W, where W is the evaporation energy. The mean distance of travel of the adsorbed molecules between the time they hit the surface and evaporate again is given by

$$x_s = ae^{(W_s'' - V_s)/kT}$$

where V_s is the activation energy for surface diffusion (which is estimated to be 1/20 W) and W_s' is the evaporation energy from the surface to the vapour (estimated to be 3 ϕ or W/2). Then

$$x_s = ae^{3\phi/2kT}$$

and when $\phi/kT = 4$, x_s has a value of 4×10^2a. This shows that particles diffuse over considerable distances before evaporation. The number of particles which arrive at a given point on the surface by diffusion are then greatly in excess of those which arrive by deposition from the vapour.

The particles adsorbed on the surface layer diffuse towards the kinks. At equilibrium the rates of departure and arrival at the kinks are equal. The rate of departure depends on the temperature and the rate of arrival on the vapour concentration.

The surface concentration away from the growing step is N_α and this is equal to $N_0\alpha$ where α is the supersaturation ratio and N_0 is the equilibrium concentration which is also assumed to be the concentration at the step

$$N_0 = \frac{1}{a^2} e^{-W_s/kT} .$$

The smallest distance from the step at which the concentration is N_α would be the mean diffusion distance x_s. The concentration gradient is then $\frac{(N_0\alpha - N_0)}{x_s}$. The rate of advance of the step, v, is a^2 times the number of particles arriving at 1 cm. of edge per second.

$$v = a^2 . 2 . D . \frac{(N_0 \alpha - N_0)}{x_s}$$

where a^2 is the area occupied by one molecule and D is the surface diffusion coefficient. The factor of 2 is required since molecules can move in both directions towards the step.

The Einstein equation for Brownian motion gives

$$x_s^2 = D \tau_s$$

where τ_s is the average length of time the molecule is adsorbed on the surface before evaporation. Frenkel (34) gives the value of τ_s as

$$\frac{1}{\tau_s} = \nu e^{-W_s'/kT}$$

where ν is a frequency factor of the order 10^{13} $\sec^{-1}$ for monatomic substances. Combining the Einstein and Frenkel equations gives

$$D = x_s^2 \nu e^{-W_s'/kT}$$

from which

$$v = 2 (\alpha - 1) x_s \nu e^{-W/kT} .$$

A curved step with a radius of curvature r advances with a rate ν' given by

$$\nu' = \nu\,(1 - r_c/r)$$

where r_c is the critical radius of curvature given by

$$r_c = \frac{a\phi}{2\ kT\ln\alpha}\ .$$

This suggests that steps will grow at an appreciable rate at low supersaturation ratios until the layer becomes smooth. For continued growth after this a new layer must be nucleated. Growth should then be periodic - fast for the completion of a stepped layer, slow for the nucleation of a new layer. The experimental observations made on crystal growth did not appear to agree with the theory.

To account for structure sensitive properties of crystals such as plasticity and crystal strength, imperfections in ideal crystals have been introduced. These defects are such things as lattice vacancies, incorporation of foreign substances into the crystal lattice and dislocations.

The first type of dislocation, introduced by Taylor (92), Polanyi (80) and Orowan (76) is an "edge dislocation." Fig. 4 represents a block of crystal in which the upper half has been pushed in the direction of the arrow. The section ABCD has slipped in the direction of the arrow while the section CDEF has not moved. The line CD marks the boundary between the regions which have slipped by different amounts and is called the dislocation line. In the upper half of the crystal the atoms are compressed and in the lower half they are extended. The dislocation line lies at the edge of the plane separating the compressed section from the extended section and it is at right angles to the slip

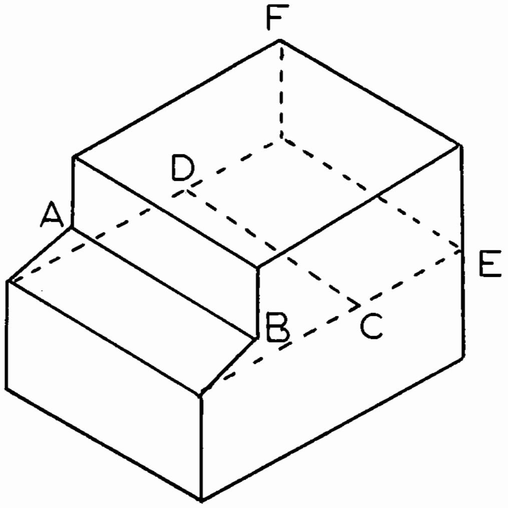


FIG. 4
An Edge Dislocation.

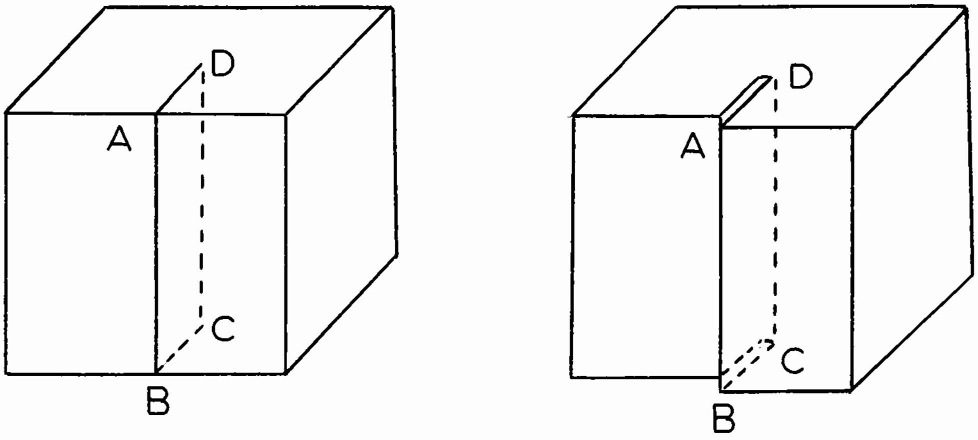


FIG. 5
A Screw Dislocation.

direction.

A second type of dislocation, introduced by Burgers (18) is a screw dislocation (Fig. 5). A cut ABCD is made in a crystal part way through it. One side of the cut is pushed down and a step is created on the surface of the crystal. The line CD is the boundary between the parts of the crystal which have slipped by different amounts and is, then, a dislocation line. This screw dislocation may be either right handed or left handed depending upon which side of the cut in the crystal is displaced downward. This is the type of dislocation which is of importance for crystal growth theory.

The step created by the screw dislocation is not the same height over its entire length. Burton, Cabrera and Frank (19) have suggested that when molecules or atoms are adsorbed along such a step, the step will persist throughout growth and will not disappear as in the case of a simple step. The result is that growth can continue without the nucleation of new layers and hence growth can continue at low supersaturation ratios. If growth occurs in this way pyramidal growth spirals should occur on a crystal face. These spirals have indeed been observed and Verma (94) has given a thorough discussion of these.

Burton, Cabrera and Frank have calculated the shapes and radii of curvature which these growth spirals should have.

There are a number of possibilities for the origin of screw dislocations: a thin crystal may buckle under its own weight during growth; the crystal may adhere to a solid which already possesses such a dislocation; two growing crystals may grow together out of coincidence; the growing crystal may collapse into vacant lattice sights. Experimental evidence seems to be available for all of these.

Buckley (40) tends to disagree that dislocations are the exclusive cause of growth. He contends that growth spirals are not too frequently observed and when they are, they are found only on slow growing faces. He suggested that vortices or eddies in the medium surrounding the crystal could impress themselves on the crystal surface and account for the observed spirals.

Gomer and Smith (39) have suggested that crystal surfaces can become mechanically stressed due to the unequal attractive forces operating on the atoms in the surface layer. These stresses are removed by a mechanical equilibrium which is not necessarily attained with thermodynamic equilibrium. The relief of these surface stresses can occur by a disruption of the lattice regularity at the surface and this should be the case with slow growing crystals which can reach the mechanical equilibrium. The net results are that fast growing crystals should have the more perfect faces since there is no chance for the surface disturbances, caused by mechanical equilibrium, to distort the lattice and the nucleation of new layers on a slow growing crystal should occur at the surface disturbances without the necessity of screw dislocations.

At the moment, however, the dislocation theory appears to have gained widespread acceptance as the most probable method of growth.

CRYSTAL FORM AND HABIT MODIFICATIONS

The study of the growth of crystals has allowed the development of theories of crystal growth which more or less correlate theory and fact. These theories of growth contribute little or nothing to the understanding of why a crystal assumes the form it does or why a crystal under varying conditions can assume a variety of habits.

Wells (97) has summarized the types of variation in crystal habits as follows:

(a) faces of the same form may be developed to different extents, e.g. cubes becoming needles or plates.

(b) on a crystal showing two or more forms it may be possible to vary the relative areas of the faces of the different forms.

(c) faces of a new form may appear.

He considered variations of the first type to be due to accidental causes. For example rapid growth, in general, leads to extreme development and under such conditions needles and plates appear frequently. It is well known that the change of a solvent in which crystallization is brought about often results in a habit modification of the crystal. No systematic study of this appears to have been made, indeed, often such modifications are known but not recorded. This is particularly so with organic materials.

The presence of impurities in a solution frequently brings about a change in the habit of growing crystals. Experimentally it has been found that the most prominent faces on a crystal are those which grow most slowly. It has been suggested that impurities may be preferentially adsorbed on certain faces and thus prevent their growth. The result is that these faces predominate in the final crystal. Solvents may act as such impurities and different solvents may be adsorbed on different faces resulting in habit modifications. In contrast to this Buckley (13) has shown that in a number of cases, crystals have been modified by the presence of dyes but that the dyes were not adsorbed on the faces which were modified. Different concentrations of impurity often have different modifying effects.

It would appear that an adequate theory of crystal habit modification must be concerned with (a) the choice of planes on which growth occurs, (b) the relative rates of growth of planes, (c) the mechanism of effects caused by impurities. Some attempts have been made to explain equilibrium shapes of crystals and those of Curie and Wulff have been mentioned above.

Bravais (9) related the velocities of growth of crystal faces to the densities of lattice points in the planes (reticular densities). He showed that the planes of maximum density would extend slowly in a direction perpendicular to the plane. These planes would then extend parallel to themselves so as to annihilate the more rapidly growing planes. Niggli (73) extended this idea and calculated the thickness of a layer which contained all the atoms whose valences were only partially satisfied. The growth rates of various planes were related to the thickness of these planes which contained all these atoms of unsatisfied valences. The results obtained were in slightly better agreement with experimental observations than the results obtained with the simple Bravais theory.

Donnay and Harker (27, 28) have drawn up a list of planes, for a given crystal, in order of decreasing distance between the planes. The position of a plane in this "morphological aspect" is a measure of its importance relative to the other planes. The agreement between this and observations is good in many cases but there is a large number of disagreements.

Reticular density theories are open to these objections (98):

(a) they imply that the habit is affected only by coplanar atoms.

(b) they do not predict which combination of atoms results in the most stable surface if two kinds of atoms are present.

(c) they neglect all influences which the environment of the crystal may have.

If a face has the lowest surface free energy and if a series of such faces enclose a volume it would be thought that this face would occur exclusively on the crystal. Wells (99) has shown that this is not the case. Fig. 6 shows the change from a cube to an octahedron by the superimposing and development of 111 faces.

Let a be the length of the edge of the cube, y the length removed to form the 111 faces, σ_{100} and σ_{111} the specific surface free energies of the 100 and 111 faces respectively. The volume of Fig. 6b is given by

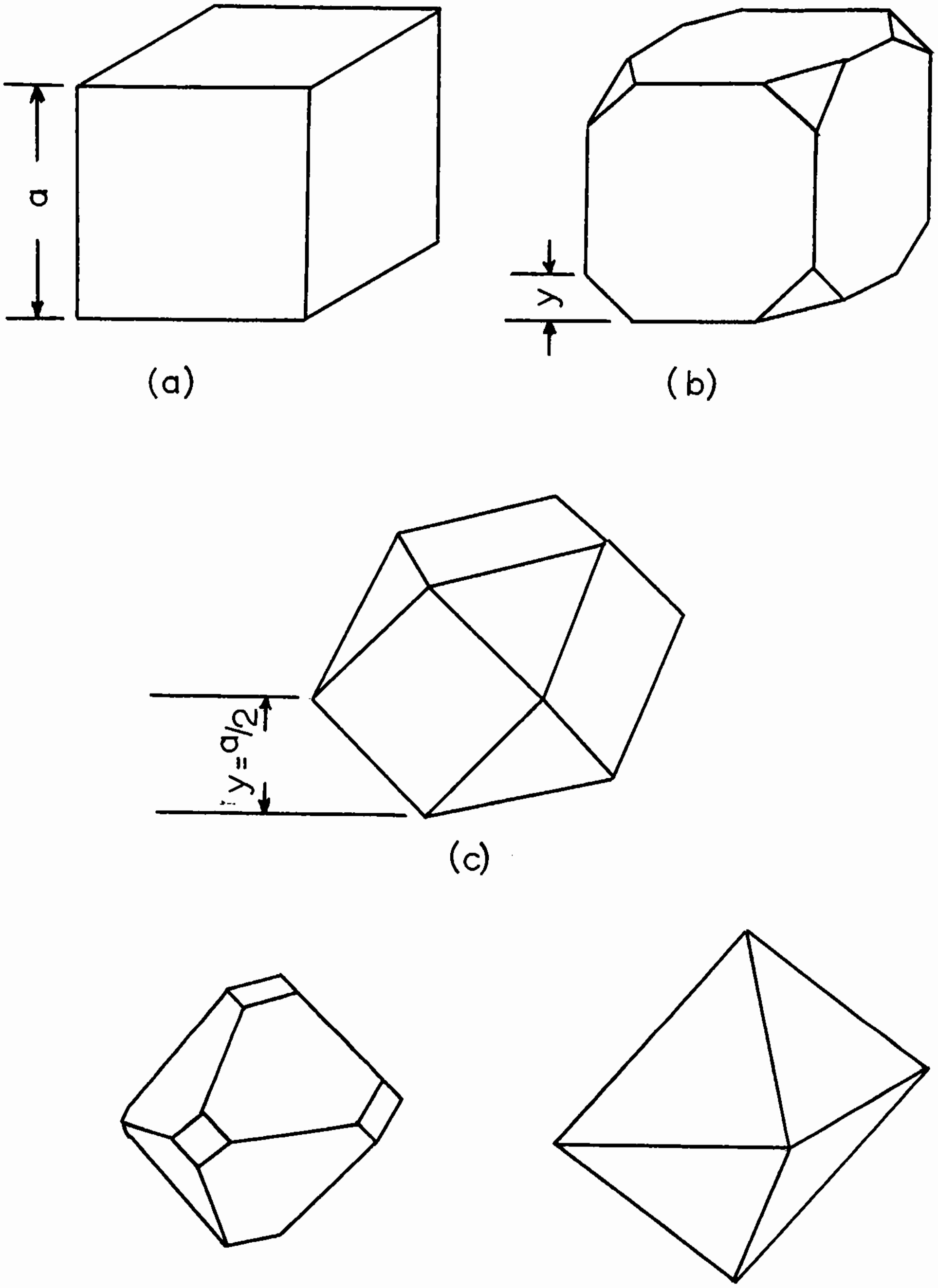
$$V = a^3 - \frac{4y^3}{3}$$

and the total surface free energy, F, is given by

$$F = 6(a^2 - y^2)\sigma_{100} + 4\sqrt{3}\,y^2\sigma_{111}.$$

For an equilibrium crystal

$$\frac{\partial F/\partial a}{\partial V/\partial a} = \frac{\partial F/\partial y}{\partial V/\partial y}$$



(a) (b)

(c)

(d) (e)

FIG. 6

Change of a cube to an octahedron.

hence $$\frac{12\,a\,\sigma_{100}}{3a^2} = \frac{-\,24\,y\,\sigma_{100} + 8\sqrt{3}\,y\,\sigma_{111}}{-\,4y^2}$$

and $$y/a = \frac{3\,\sigma_{100} - \sqrt{3}\,\sigma_{111}}{2\,\sigma_{100}}\ .$$

When $y = 0$, σ_{111} is equal to $\sqrt{3}\,\sigma_{100}$ which means that if σ_{111} is greater than 1.73 σ_{100} the equilibrium shape is a cube. When $y = a/2$, σ_{111} is equal to $2\,\sigma_{100}/\sqrt{3}$ and this represents the condition for the growth of the cubo-octahedron (Fig. 6c). When $\sigma_{111}/\sigma_{100}$ lies between $\sqrt{3}$ and $2/\sqrt{3}$ the equilibrium form of the crystal would be similar to Fig. 6b. Similarly it can be shown that the octahedron is the equilibrium shape when σ_{111} is equal to or less than $\sigma_{100}/\sqrt{3}$. The results of this treatment are summarized in Table II.

Table II

Equilibrium shape	Range of $\sigma_{111}/\sigma_{100}$
Cube (Fig. 6a)	$\geqslant 1.73$
Fig. 6b	$< 1.73 \; > 1.15$
cubo-octahedron (Fig. 6c)	1.15
Fig. 6d	$< 1.15 \; > 0.58$
octahedron (Fig. 6e)	$\leqslant 0.58$

Absolute values of these surface free energies are not known. Herring (37) gives some calculated values of these for a few crystals. For the diamond σ_{100} is given as 9820 ergs per square centimetre and σ_{111} as 5650 ergs per square centimetre. The ratio $\sigma_{111}/\sigma_{100}$ is then 0.57 and the equilibrium form should be the octahedron. For tungsten the ratio $\sigma_{111}/\sigma_{100}$ is 1.04 hence the equilibrium shape should be similar to Fig. 6d.

One difficulty with this treatment of habit modification is that the surface free energies would be affected by the solvent used and by the presence of impurities. As yet there seems to be no means of taking these into account.

The screw dislocation theory of crystal growth can account for some habit modifications by impurities. If the impurity is adsorbed at the dislocation the growth rate would be affected and this should lead to habit modification. Sears (86) has recently attempted to explain the growth of metallic whiskers or needles from the vapour phase in terms of a single screw dislocation at the tip of the growing whisker.

The following observations have been made on crystal habit modification and these must be accounted for by any theory which is to be at all successful:

(a) the solvent used and the presence of impurities often affect crystal habits.

(b) there seems to be no relationship between the relative solubilities of the crystallizing substance and impurities and the habit modification of the crystal.

(c) the same impurity in different concentrations may have different modifying effects.

(d) crystals grow more regularly with lower supersaturation.

(e) crystals grown at high temperatures appear to be more perfect than those grown at low temperatures.

(f) dendrites occur when the growth rate is rapid but rapid growth does not always produce dendrites.

(g) the habit of a crystal becomes more complex with a slower rate of growth.

The following are the observed facts on crystal growth:

(a) growth appears to start on the interior of a crystal face and spread to the edges.

(b) a metastable region of supersaturation appears to exist before crystallization occurs.

(c) the rate of nucleation appears to be a function of the supersaturation (8).

(d) evidence appears to be contradictory as to whether or not the rate of growth is influenced by the degree of supersaturation.

(e) different faces of a crystal may grow at different rates.

(f) flawed surfaces grow more quickly than smooth surfaces.

(g) twinning is more apt to occur with greater degrees of supersaturation (16).

An adequate theory of crystal habit modification must account for all of these observations. As yet no such theory seems to have been devised.

Egli and Zerfoss (31) suggested that impurities may increase the range of supersaturation over which spontaneous nucleation is inhibited and that this should lead to more perfect crystals. This is in contradiction with the observation that more perfect crystals grow at low supersaturations.

Nakaya (72) developed a technique for growing snow crystals from water vapour. By measuring the temperature of the water vapour and the cold surface on which the crystals grew he estimated the extent of supersaturation. A plot of percent supersaturation and temperature of crystal growth was made for the various types of crystals formed (Fig. 7). This graph shows that dendrites tend to grow at high supersaturations and simple forms at low supersaturations. A given crystal form grows within a wide range of supersaturation but within a relatively narrow temperature interval. This indicates that the temperature at which the crystal is formed and grows has more influence on the crystal habit than the degree of supersaturation. Nakaya also asserted that the rate of growth of a crystal, which is governed by the degree of supersaturation, influenced the crystal habit.

Mason and his co-workers (61) have extended the observations of Nakaya into regions of higher supersaturation and they obtained the same basic plot of supersaturation and temperature of crystal growth but there were a few differences (Fig. 8). These have found the temperature boundaries to be quite sharp. They concluded that the crystal habit is influenced primarily by the temperature at which growth occurs, that growth rates are influenced by supersaturation and that supersaturation governs the development of secondary features on crystals, e.g., needlelike extensions on prisms and at the corners of plates. Mason (62) suggested that a thermodynamic phenomenon, which is dependent upon the relative free energies of growth in different habits, is involved in view of the sharp changes in crystal form with temperature.

The excess of ambient vapour density over the vapour density in equilibrium with ice crystals at their own temperature governs the type of crystal formed in snow is the view of Marshall and Langleben (60). Changes in crystal type occur when this vapour density excess is sufficient to overcome the inhibitions to growth at the corners and edges of crystals.

Temperature has only a minor influence on crystal habit is the opinion of Buckley (14). It acts by accelerating evaporation thus speeding up deposition which in turn will tend to simplify the crystal habit. This observation was made with static systems and does not

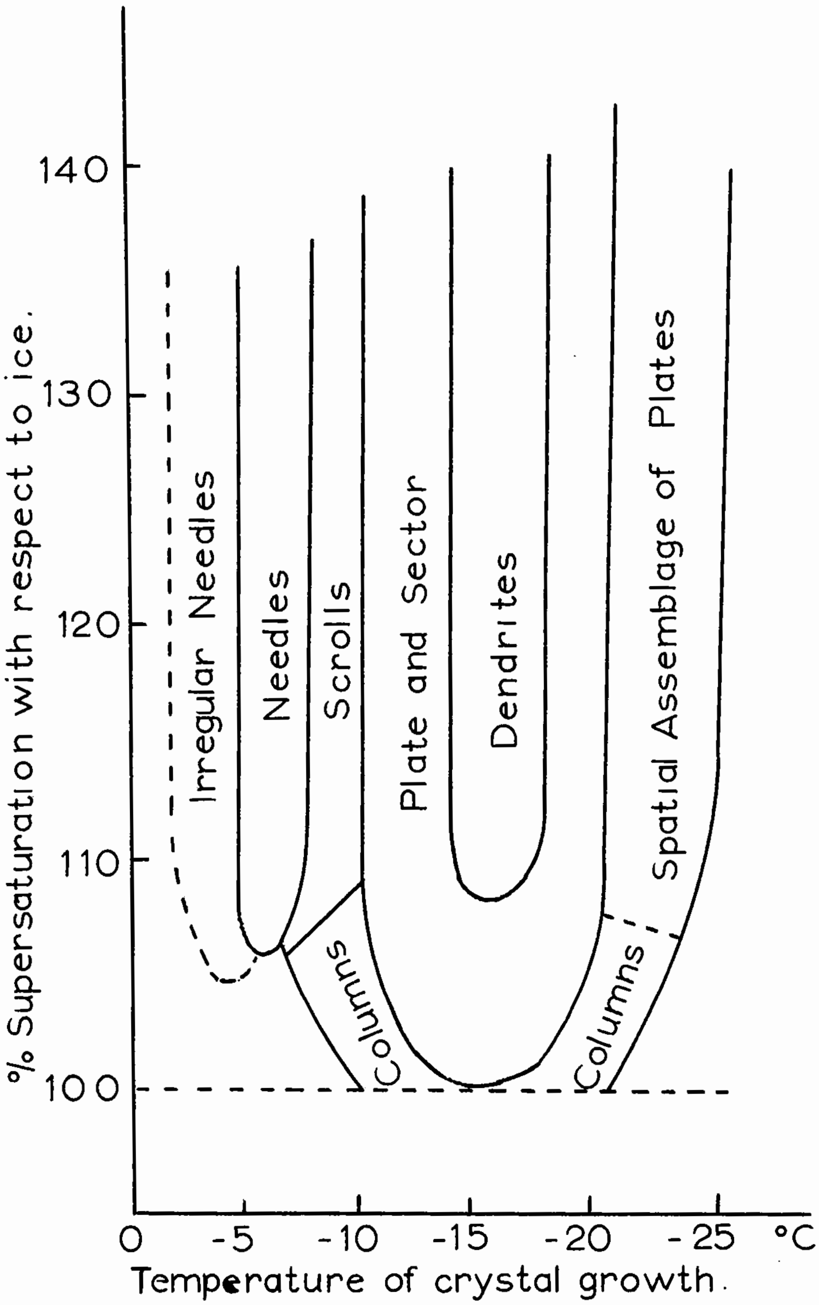


FIG. 7

% Supersaturation vs temperature of crystal growth.

After Nakaya (72)

% Supersaturation vs temperature of crystal growth

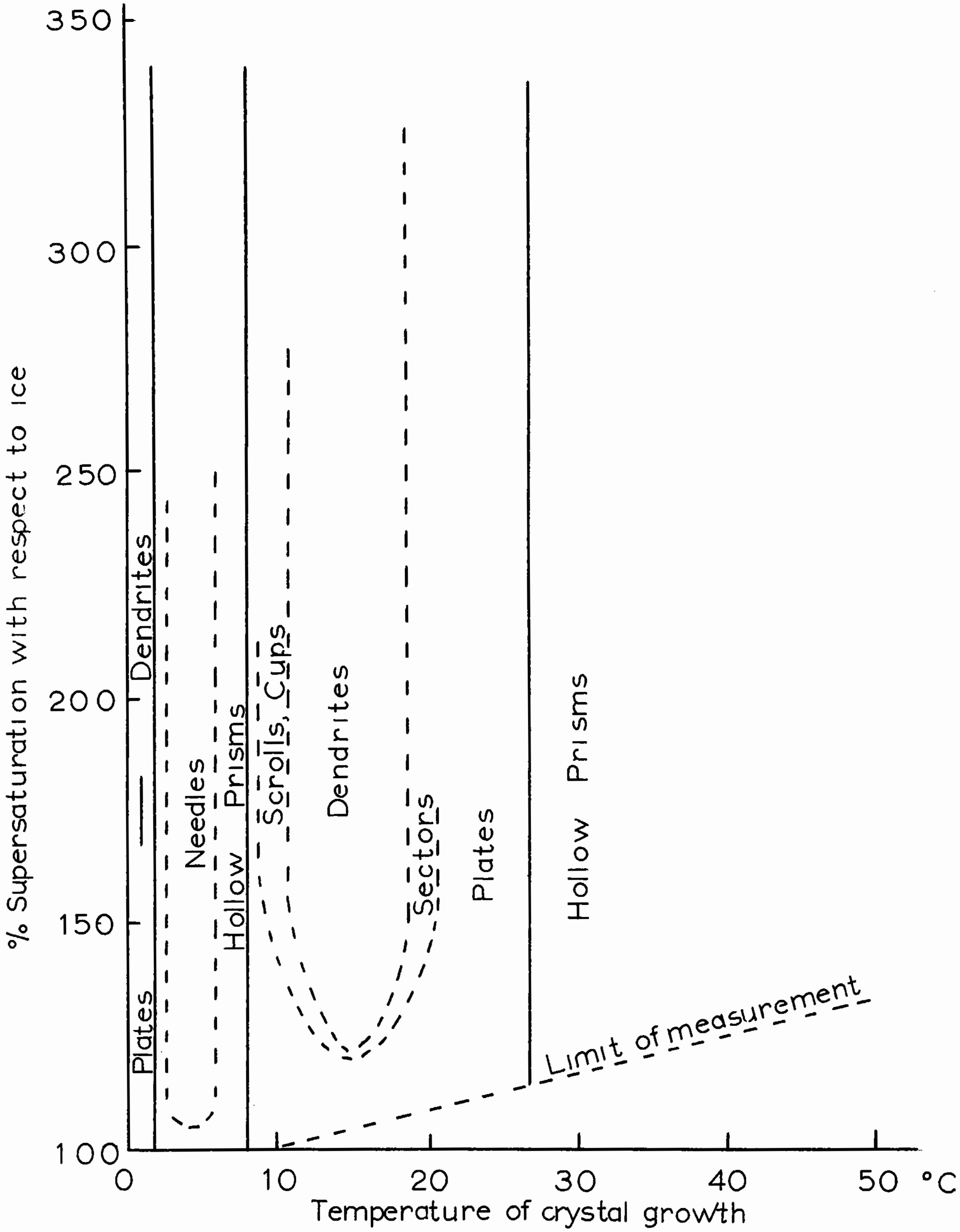


FIG. 8

After Mason (61)

necessarily apply to a dynamic system.

Mokievski (70) reported that in the growth of $MgSO_4 \cdot 7\ H_2O$ crystals under dynamic conditions the supersaturation had no influence on the shape of the crystal but under static conditions the shape was affected.

The formation of silver crystals by the reduction of silver ions with ferrous ions was studied by Courtney (20). Plates and needles were formed. The rate of needle growth was found to be independent of the supersaturation. Whisker growth was attributed to a single screw dislocation. Sears (85) also attributed the growth of mercury whiskers from the vapour phase to a single screw dislocation and the growth of plates to two screw dislocations at right angles.

THE CRYSTAL HABITS OF THE COINAGE METALS (25)

The three coinage metals, copper, silver and gold, have face-centred cubic lattices. They form crystals which belong to the cubic system but well developed crystals are rarely found naturally. Bjornstahl (6) claimed to have found crystals of gold which belonged to systems other than the cubic but this claim has never been verified by others.

Copper has been reported to occur as cubes, dodecahedra, octahedra and combinations of these. Silver occurs as cubes, dodecahedra, octahedra, hexakisoctahedra and combinations of these. Gold occurs as cubes, dodecahedra, trapezohedra and combinations of these. All three occur in dendritic forms and filiform or twisted wire shapes. Needles and plates have also been observed. Twinning is common with all three of these metals.

Hexagonal plates of gold with triangular spiral markings were reported by Amelinck, Grosjean and Dekeyser (2). Powdered silver prepared by electrodeposition has been found to have some microscopic six-sided stellate crystals (65).

SCOPE AND PURPOSE OF THE INVESTIGATION

Very few data are available in the literature on the crystal habits of substances formed as a result of a chemical reaction in solution. Still fewer data are reported for crystals of metals grown as a result of such chemical reactions. This investigation was originally undertaken to determine some of the factors which influenced the crystal habit of metallic copper formed as a result of a reaction in solution and in time the investigation was extended to include the other coinage metals, silver and gold.

The reversible reactions outlined above were considered to be the most practical methods of forming the crystals. These choices of reactions made it necessary that the experimental apparatus be constructed with provisions for heating a solution in contact with the metal in massive form and then cooling it in order to reverse the reaction. Since the prime purpose of the investigation was the observation of variations in crystal habits it was necessary to remove the hot solution from contact with the massive form of the metal in order that this would have no effect on crystals formed by reversing the reaction.

As a result of these requirements a dynamic system was needed. The liquids to be circulated were known to be corrosive hence a pump could not be used for circulating them. A system was then designed which used the difference in densities between hot and cold solutions as a driving force and which also included a means of separating and removing the crystals formed by the chemical reaction.

The solutions chosen to be circulated were of two types: simple acids and solutions containing a metallic cation capable of oxidizing the massive form of the metal. The choices eventually made are discussed above in the section on chemical reactions.

In the discussion on crystal habit modifications it may be noted that the presence of foreign substances often has a modifying effect on crystals. Some experimental runs were planned using other electrolytes in the circulating solution in addition to the reagent used to attack the massive form of the metal in order to examine this aspect of habit changes. This was actually carried out only in the case of copper.

The literature shows that the viscosity of the medium in which crystallization is occurring sometimes has an influence on the shape assumed by the crystals. To study viscosity effects some solutions containing different amounts of glycerine were circulated.

A literature survey showed that in other systems involving the formation of crystals the temperature of crystal growth and the degree of supersaturation appeared to influence the habits of the crystals which were grown. There appeared to be some disagreement among various workers as to which of these factors was the more important. A technique, described below, was developed to examine the effect of these variables in the systems which were studied.

In addition to the main objective of examining some of the factors influencing crystal habit it was thought that other data obtained easily during the course of the work might lead to some interesting results. The rate of production of crystals, the size distribution of crystals obtained and their shape distribution were accordingly determined during some experimental runs. Another variable investigated was the effect of the duration of the run on habit, rate of production of crystals and their size and shape distributions.

EXPERIMENTAL PROCEDURES

The apparatus used in the experimental work is shown in Fig. 9. It consisted of a reaction flask, A, which was a 125 ml. Erlenmeyer flask with an extension added to the neck. The extension was equipped with a cold finger condenser which fitted snugly but not too tightly into the neck of the flask. On the side of the flask, near the neck, a side arm of 15 mm. outside diameter tubing was added. This in turn was attached to a vertical piece of tubing, of the same diameter, about 80 cm. in length. This upright tube was surrounded with a cooling condenser, B, 58 cm. in length, placed about 8 cm. below the point of attachment of the side arm on the reaction flask. At the outlet of the condenser the tubing was reduced to 8 mm. external diameter. This was attached tangentially to an inverted 125 ml. Erlenmeyer flask, D, which served as a cyclone type collector. The neck of this flask was attached to a wide bore stopcock.. A piece of 8 mm. outside diameter tubing about 80 cm. long was attached to the centre of the top of the collector. A second condenser, C, surrounded this tubing and it was placed 15 cm. above the top of the collector. This condenser was 46 cm. in length. A side arm was attached to this upright tube about 19 cm. from the top of condenser C. The side arm led into the centre of the side of collector E. The collector E was made of a piece of 25 mm. outside diameter tubing about 13 cm. in length. Pieces of 8 mm. outside diameter tubing were attached to the top and bottom and the lower section contained a stopcock. The upper piece of small diameter tubing was attached to the reaction flask, A, near the bottom by a piece of 8 mm. outside diameter tubing. During the operation of the apparatus the top of the three upright tubes were

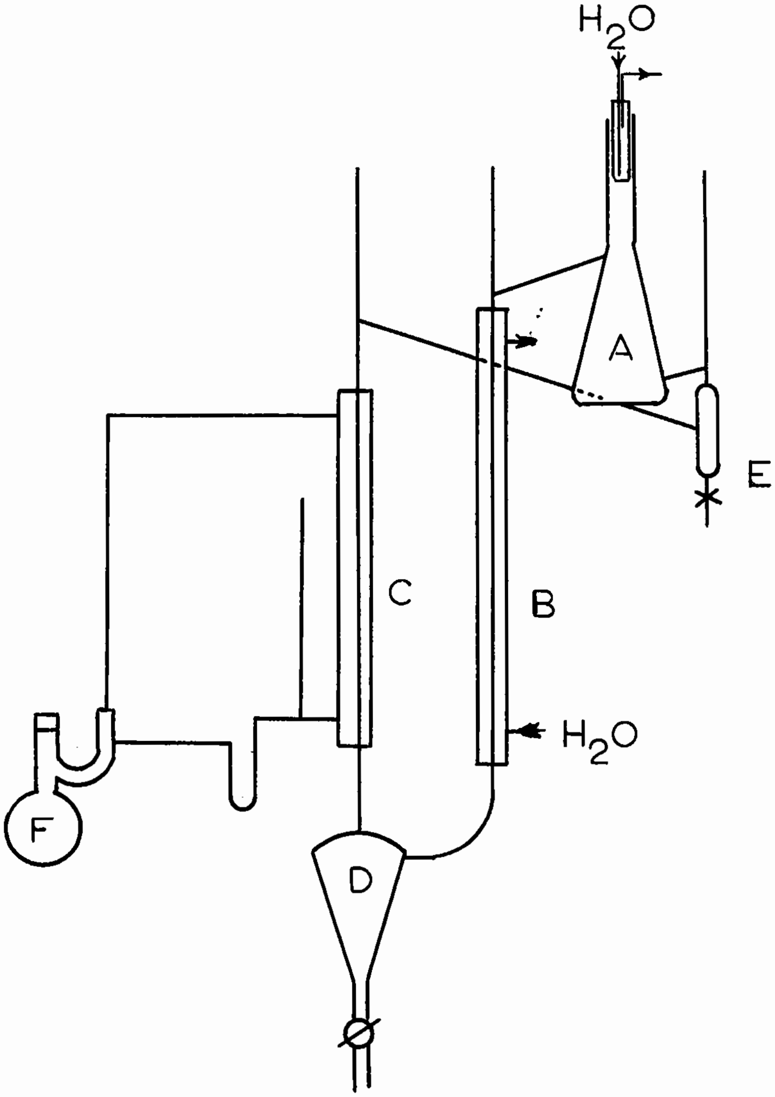


Fig. 9

Diagram of apparatus

(Not to scale.)

stopped with corks.

A 125 ml. Claisen flask served as a steam generator. The second neck of the flask was attached to the top of condenser C with 8 mm. external diameter tubing. The bottom of condenser C was attached to the side arm of the Claisen flask by a piece of 8 mm. tubing containing a trap and an upright vent. The first neck of the flask was fitted with a rubber stopper. This arrangement allowed steam to pass into the condenser C and heat the contents of the upright tube. The condensed steam was returned to the boiler F through the trap. In this way steam could be generated continuously without refilling the boiler. The vent was put in for safety purposes so that the system would not be closed.

The massive metal in the form of wire was placed in the reaction flask A and the solution which was to react with the metal was put into the apparatus until it was full. The flask was heated and the chemical reaction between the metal and solution began. The solution was circulated through the system by the difference in its density between the cooling section B and the heating section C. In the cooling section the chemical reaction occurring in flask A was reversed and crystals of metal separated out. These crystals were gathered in the collectors D and E.

When a sufficient quantity of crystals had been formed they were withdrawn through the stopcocks with the circulating liquid. The mixture was filtered with suction on sintered glass funnels, the crystals were washed with water and then methanol. These were then dried at 110°C and weighed to determine yields.

The apparatus was cleaned between runs with nitric acid in the cases of copper and silver and with aqua regia in the case of gold. After treatment with acid the apparatus was washed out three or four times with distilled water and then the new run was started.

A technique of growing crystals on a thread was used to determine the effect of temperature on the habit of crystals. A thread was hung in the centre of the cooling tube B and this was weighted by means of a thermometer. A thermometer was inserted in the top of the tube so that its bulb was at the top of the section just in the condenser B. These two thermometers registered the temperatures at the top and bottom of the cooling section. The length of thread was measured. After a period of time the thread was withdrawn and cut into sections approximately one quarter of an inch in length and these were mounted on microscope slides for examination.

Immediately upon withdrawal of the thread with crystals a second thread, attached to the same thermometer was introduced into the cooling tube. This was gradually lowered further into the tube. The distance from the top of the tube and the temperature were recorded and these data were used to plot a cooling curve of temperature vs. distance from the top of the tube.

The sections of thread containing crystals were measured and segments of the cooling curve were cut off corresponding to the length of each section, starting from the lowest point on the curve. Thus it was possible to estimate the temperature at the inlet and outlet of each thread section. These data allowed the determination of the temperature drop across each section and the average temperature of each section.

Microscope slides were prepared for examination by mounting the material in Fisher Permount. Slides were made from thread sections and also from samples of the crystals gathered at the collectors D and E.

Each thread section was examined for the forms of crystals which appeared on it. For each type of crystal a plot was made of the temperature drop across the section vs. the average temperature for the section on which the form first made its appearance. Later, it was found more useful to plot the reciprocal of the temperature drop in place of the temperature drop itself.

The relative proportions of the various forms were determined using the slides made from the samples gathered at the collectors. This was done by counting the numbers of each form present in random fields of the slides as observed under the microscope. A minimum of one thousand counts was made for each slide observed.

Size distributions of the crystals grown on threads were only made qualitatively. The collector samples were passed through seives and the percentage retained on each was determined by weighing. The distribution of smaller sizes was determined by projecting random fields of the slides, as seen through the microscope, onto a calibrated grid by means of a mirror arrangement. The grid was made by projecting a calibrated slide onto a sheet of paper using the same mirror arrangement. The grid was thus divided into squares of known area. The sizes of the crystals were estimated by the number of squares covered on the grid. As above, a minimum of one thousand counts was made for each slide.

Analyses of the circulating solutions were done by standard methods. The total equivalents of anion were determined, the total equivalents of cation were determined and the difference between these was taken as the equivalents of hydrogen ion. The crystals were analysed by dissolving them and plating the metals out again electrolytically.

Photographs were taken with a Polaroid Land camera.

EXPERIMENTAL RESULTS

Three similar sets of apparatus were built and some initial tests were run to compare them. Machines A and C were run for a period of 71 hrs. with 0.5N sulphuric acid circulating. The rate of production of copper crystals was 0.028 grams per hour in both sets of apparatus. Apparatus B was also run with 0.5N sulphuric acid circulating but the duration of the run was 119 hours. The rate of production of crystalline copper was 0.036 grams per hour. The increase in rate is attributed to the increased duration of the run (see Discussion below). Apparatus A was run for 47 hours with 3N sulphuric acid and apparatus B for 48 hours with 3N sulphuric acid also. The rate of production of crystals in apparatus A was 0.027 grams per hour and the rate in apparatus B was 0.024 grams per hour. These results show that the various experimental arrangements had similar operating characteristics.

Where possible, the experimental results are presented graphically and in order to avoid filling this section with numerous tables, on which the graphical results are based, these tables have been assembled in Appendix A.

Yields. Fig. 10, based on Table III, shows the yield of crystalline copper obtained when sulphuric acid was the circulating liquid. Other acids were not used as they do not permit the desired reaction to occur. Fig. 11, based on Table IV, shows the yields of copper crystals obtained when solutions of 0.1M cupric sulphate in 0.1N sulphuric acid were circulated. Fig. 12, based on Table V shows the yields obtained when other solutions of cupric sulphate in sulphuric acid were used.

Solutions of various sulphate salts in sulphuric acid were

Table III

Yields of Copper with H_2SO_4 circulating

Run No.	Acid Conc.	Duration (hrs.)	Cumulative Hrs.	Yield (gms.)	Cumulative Yield (gms.)	Rate of Prod. (gms./hr.)
A4	3N	47	47	1.1452	1.1452	0.027
B2	3N	48	48	1.0872	1.0872	0.024
A3	1N	48	48	1.0727	1.0727	0.022
A1	0.5N	71	71	1.9872	1.9872	0.028
B1	0.5N	119	119	4.3037	4.3037	0.036
C1	0.5N	72	72	1.9996	1.9996	0.028
B13	0.5N	24	24	0.5312	0.5312	0.020
		24	48	1.0714	1.6026	0.033
		24	72	1.1691	2.7717	0.038

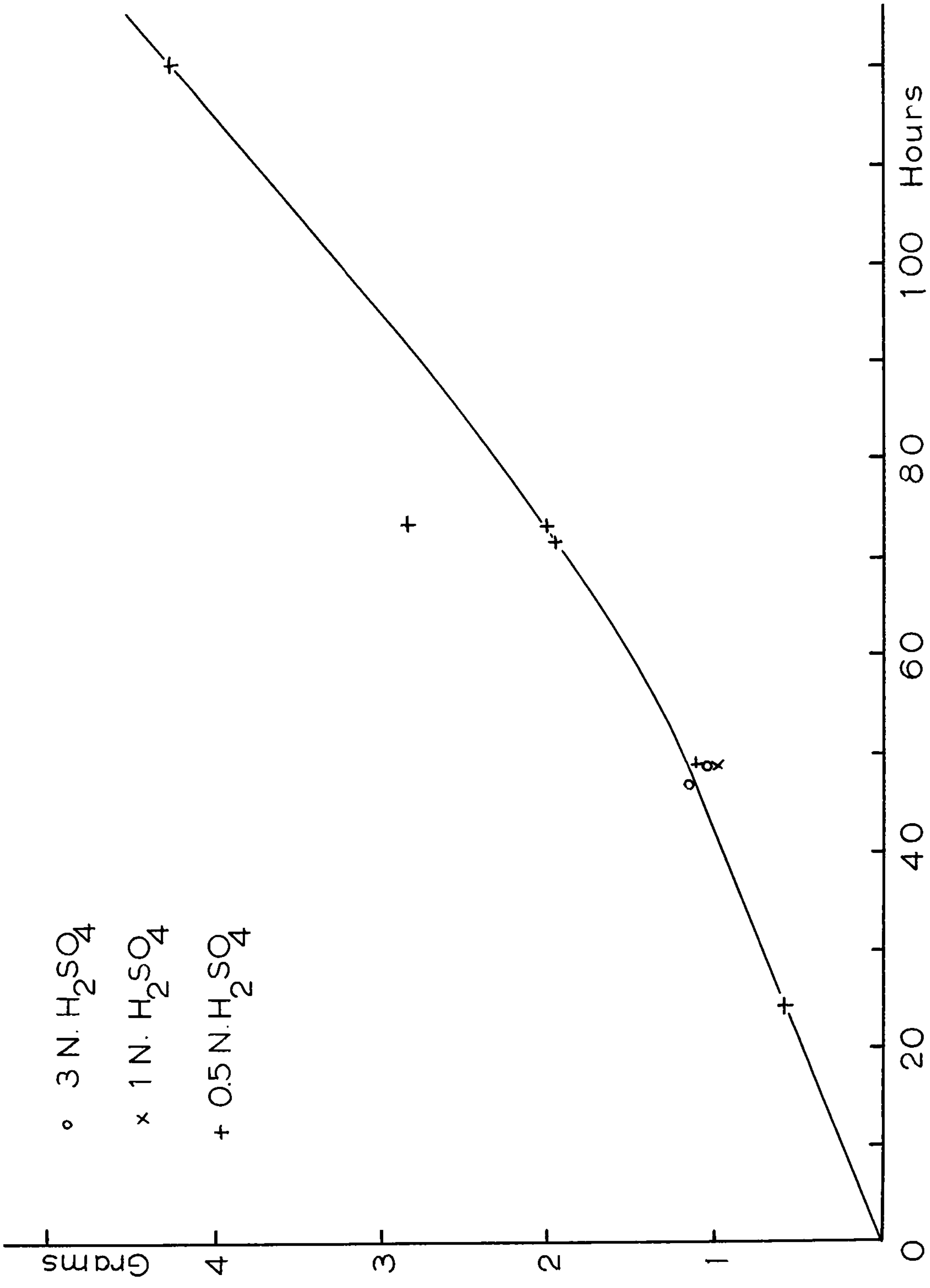


FIG. 10

Yields of copper with H_2SO_4 circulating.

Table IV

Yields of Copper with 0.1M $CuSO_4$ in 0.1N H_2SO_4 circulating

Run No.	Duration (hrs.)	Cumulative Hrs.	Yield (gms.)	Cumulative Yield (gms.)
A10	96	96	7.1904	7.1904
B9	48	48	7.1618	7.1618
C10	48	48	4.9704	4.9704
C11	96	96	7.2912	7.2912
C12	72	72	7.9012	7.9012
C13	24	24	1.6528	1.6528
	23¾	47¾		3.4061
		70¾		5.0860 *
		96		9.9352
		120		12.8816
		148		13.4342
		170		13.8117
		194		14.2337
		218		14.2337
D1	3½	3½	0.2862	0.2862
D2	4	7½	0.3002	0.5864
D3	5½	13	0.4101	0.9965
D4	5¾	18¾	0.4627	1.4592
D5	6½	25¼	0.5492	2.0084
D10	6	6	0.4827	0.4827
D13	5	11	0.4186	0.9013
D15	5	16	0.3891	1.2904

* new wire inserted

Table IV (con't)

Run No.	Duration (hrs.)	Cumulative Hrs.	Yield (gms.)	Cumulative Yield (gms.)
D17	5	21	0.3929	1.6833
D18	4½	25½	0.3222	2.0055
D19	7	32½	0.4711	2.4766
D22	4	36½	0.4303	2.9069
D29	6	6	0.5099	0.5099
D32	6	12	0.4374	0.9473
D44	6¼	6¼	0.4592	0.4592
D47	6¼	12½	0.5166	0.9758
D49	6¼	18¾	0.4920	1.4678
D51	6½	25¼	0.5087	2.0765
D31	6	6	0.4838	0.4838
D34	6	12	0.4629	0.9467
D36	6½	18½	0.5677	1.5144
D37	6½	25	0.4804	1.9948
D39	6½	31½	0.5007	2.4955
D41	6¼	37¾	0.5163	3.0118
D43	6½	44¼	0.4897	3.5015
D46	6¼	50½	0.4074	3.9089
D48	6¼	56¾	0.5988	4.5077
D50	6¼	63	0.4833	4.9910
D52	6½	69½	0.4642	5.4552
D53	6¼	75¾	0.5399	5.9951
D54	6½	82¼	0.4111	6.4062
D55	6¼	88½	0.6066	7.0128

Table IV (con't)

Run No.	Duration (hrs.)	Cumulative Hrs.	Yield (gms.)	Cumulative Yield (gms.)
D56	6½	95	0.4629	7.4757
D57	6½	101½	0.6275	8.1032
D58	6¼	107¾	0.4373	8.5705
D60	6¾	114½	0.4807	9.0512
D62	6¾	121¼	0.5989	9.6501
D64	6¾	128½	0.5097	10.1598
D30	6	6	0.5161	0.5161
D33	6	12	0.4827	0.9988
D35	6½	18½	0.5598	1.5586
D38	6½	25	0.4378	1.9964
D40	6¼	31¼	0.5060	2.5024
D42	6½	37¾	0.4883	2.9907
D45	6¼	44	0.4272	3.4179
D59	6¾	6¾	0.5123	0.5123
D61	6¾	13½	0.5372	1.0495
D63	6¾	20¼	0.6429	1.6924

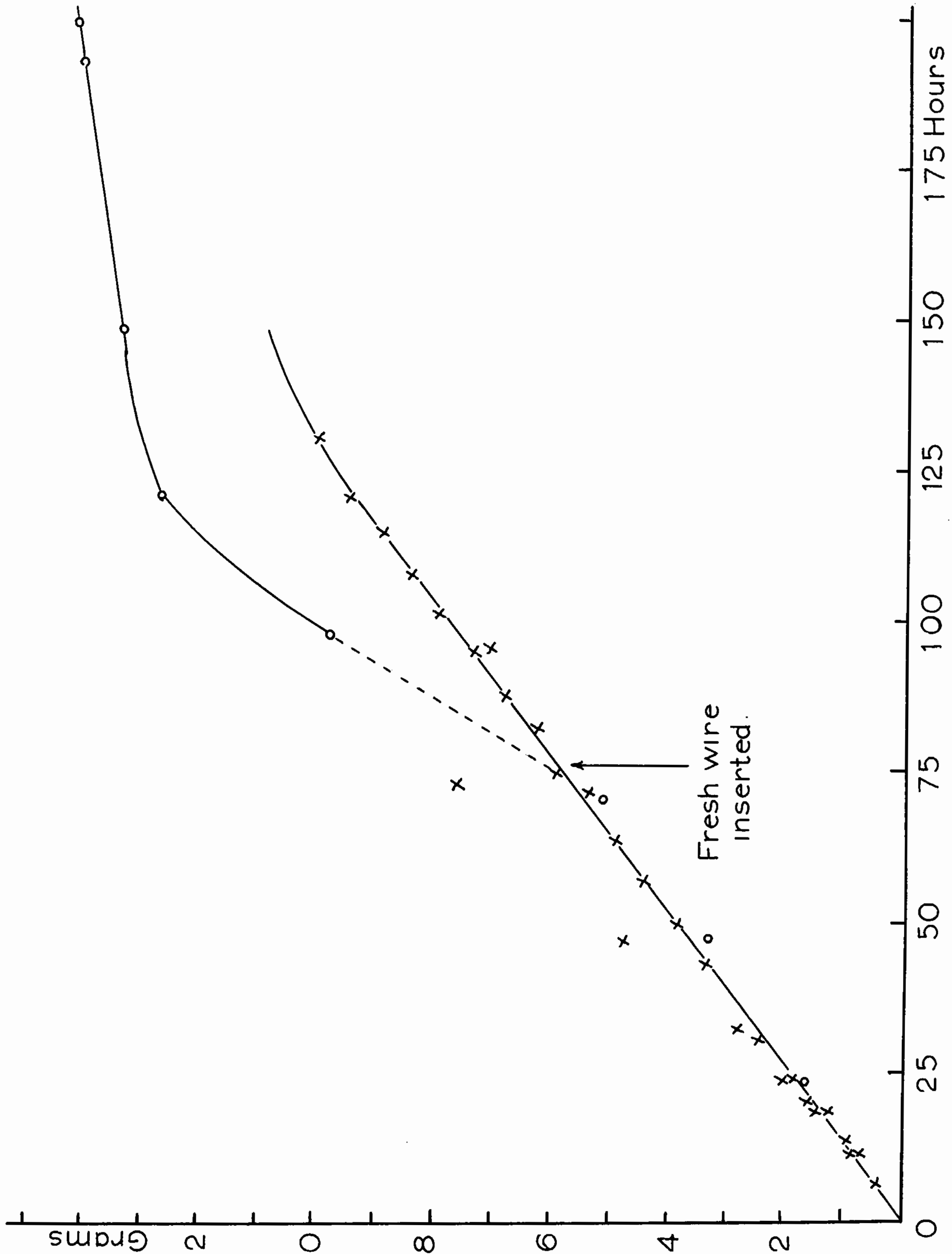


FIG 11

Yields of copper with 0·1M $CuSO_4$ in 0·1 N H_2SO_4 circulating

Table V

Yields of Copper with solutions of $CuSO_4$ in H_2SO_4

Run No.	$CuSO_4$ Conc.	H_2SO_4 Conc.	Duration (hrs.)	Cumulative hrs.	Yield (gms.)	Cumulative Yield (gms.)
A8	0.5M	0.0	48	48	2.7589	2.7589
				116	2.7589	2.7589
A11	0.5M	0.5M	12	12		2.8161
				24		6.5449
				48		11.9785
				78		18.4957
				96		25.4857
C7	0.5M	0.5N	24	24	3.9708	3.9708
C8	0.5M	1N	48	48	11.7638	11.7638
B7	0.5M	3N	24	24	7.8338	7.8338
A9	0.05M	0.5N	48	48	4.5083	4.5083
B8	0.125M	0.5N	72	72	9.6652	9.6652
C9	0.25M	0.5N	45	45	7.4228	7.4228
D28	0.1M	1N	4	4	0.3729	0.3729
D27	0.1M	2N	4	4	0.3672	0.3672
D26	0.1M	3N	4	4	0.3184	0.3184
D7	1M	1N	13	13	10.0121	10.0121
			5	18	3.8420	13.8541
			5½	23½	4.1127	17.9668
			4½	28	3.5828	21.5496
D9	0.5M	0.5N	5½	5½	1.2767	1.2767
			6	11½	1.4483	2.7250
			5½	17	1.4621	4.1871

circulated over copper wire. In all cases the acid strength was 0.5N and the salt concentrations were 0.5 mols. per litre except in the case of ceric sulphate where the concentration was 0.1 mols per litre. The purpose of this series of runs was, primarily, to observe what effect, if any, these salts had on habit modification. The yields of these runs are summarized in Table VI.

A solution of 3N sulphuric acid was circulated over silver wire and no crystalline silver was formed. Silver is soluble in nitric acid and silver chloride would be precipitated by hydrochloric acid so that these acids were not used. Solutions of ferrous sulphate in sulphuric acid did produce crystalline silver when circulated through the apparatus. Fig. 13, based on Tables VII, VIII and IX shows the yields obtained with these solutions.

The following solutions were circulated over gold wire with no crystals formed in the apparatus: 6N hydrochloric acid; 0.5N sulphuric acid; 6N hydrochloric acid containing 5 grams per litre of potassium chromate; 0.5M ferrous sulphate in 0.5N sulphuric acid and 0.5M ferric chloride saturated with bromine. This last solution and the hydrochloric acid containing potassium chromate formed metallic gold when allowed to stand for a period of time after removal from the apparatus. Solutions of ferric chloride in hydrochloric acid containing small amounts of potassium chromate were successful in producing crystalline gold when they were circulated over gold wire. The results of these experiments are summarized in Table X.

The slopes of the yield curves give the rate of production of metallic crystals.

Results of analyses of the metal crystals showed them to be pure

Table VI

Effect of Sulphate Salt Solutions on Yields of Copper

(All solutions are 0.5N in sulphuric acid)

Run No.	Salt Conc.	Duration (hrs.)	Total Yield (gms.)	Rate of Prod. (gms./hr.)
B3	0.5M $(NH_4)_2SO_4$	120	2.9260	0.025_4
C3	0.5M K_2SO_4	96	2.1172	0.027_8
C4	0.5M $ZnSO_4$	72	1.4583	0.021_8
A5	0.5M $MgSO_4$	72	0.8554	0.013_7
A7	0.5M $CdSO_4$	96	1.1565	0.014_6
A6	0.5M $Al_2(SO_4)_3$	72	1.5471	0.024_3
B4	0.5M $MnSO_4$	70	1.1001	0.018_0
C5	0.5M $CoSO_4$	70	1.6719	0.023_9
B5	0.5M $FeSO_4$	96	1.6903	0.019_9
B6	0.5M $Fe_2(SO_4)_3$	60	5.9133	0.104
C6	0.1M $Ce(SO_4)_2$	70	1.7271	0.026_8
C7	0.5M $CuSO_4$	24	3.9708	0.091_1

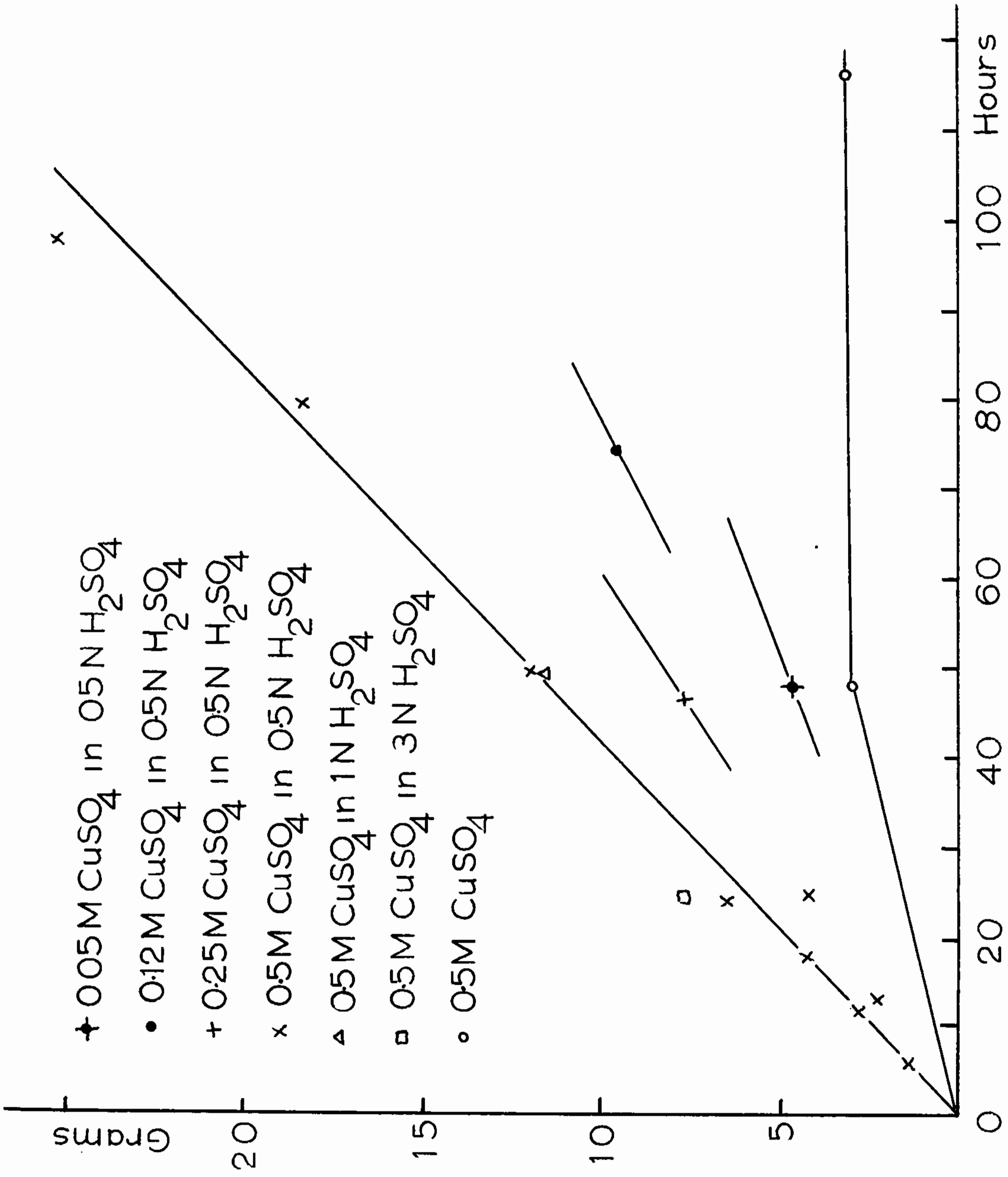


FIG 12

Yields of copper with various solutions of $CuSO_4$ in H_2SO_4

Table VII

Yields of Silver with 0.1M $FeSO_4$ in 0.2N H_2SO_4 circulating

Run No.	Duration (hrs.)	Cumulative Hrs.	Yield (gms.)	Cumulative Yield (gms.)
E33	12	12	2.0462	2.0462
E34	12	24	3.6373	5.6835
E35	6	30	2.0117	7.6952
E36	7	37	2.2874	9.9826
E37	7	44	3.0015	12.9841
E38	7	51	3.2113	16.1954
E39	6	57	2.9080	19.1035
E40	7	64	3.3441	22.4476
E41	7	71	3.4669	25.9145
E42	7½	78½	3.5772	29.4917
E43	6½	85	3.1666	32.6583
E44	7	92	3.4827	36.1410
E45	7½	99½	3.6113	39.7543
E46	7	106½	3.4991	43.2534
E47	7	113½	3.5227	46.7761
E48	7	120½	3.2701	50.0462
E49	7	127½	3.4998	53.5460
E50	7	134½	3.5203	57.0663
E51	7	141½	3.5007	60.5670
E52	7	148½	3.4983	64.0653
E16	6	6	0.2142	0.2142
E18	3	9	0.4191	0.6333
E24	13½	22½	3.0074	3.6407

Table VII (con't)

Run No.	Duration (hrs.)	Cumulative Hrs.	Yield (gms.)	Cumulative Yield (gms.)
E32	19	41½	9.0344	12.6751
E9	4	4	0.6059	0.6059
	3	7	0.4396	1.0455
	3	10	1.0653	2.1108
	3	13	0.5680	2.6788
	3½	16½	1.6753	4.3541
	5	21½	1.1862	5.5403
	4	25½	1.4251	6.9654
	3	28½	0.7135	7.6789
E14	4	32½	1.2405	8.9194
E15	6	38½	1.8907	10.8101
E17	3	41½	1.1108	11.9209
E23	13½	55	6.2438	18.1647
E29	11	66	5.6722	23.8369

Table VIII

Yields of Silver with 0.1M $FeSO_4$ in 1N H_2SO_4 circulating

Run No.	Duration (hrs.)	Cumulative Hrs.	Yield (gms.)	Cumulative Yield (gms.)
H1	7	7	0.9972	0.9972
H2	7	14	1.5037	2.5009
H3	7	21	1.9721	4.4730
H4	7	28	2.4882	6.9612
H5	7	35	2.4106	9.3718
H6	7	42	2.6033	11.9751
H7	7	49	3.0472	15.0223
H8	7	56	3.3981	18.4204
H9	7	63	3.7277	22.1481
H10	12	75	5.9021	28.0502

Table IX

Yields of Silver with 0.5M $FeSO_4$ in 0.5N H_2SO_4 circulating

Run No.	Duration (hrs.)	Cumulative Hrs.	Yield (gms.)	Cumulative Yield (gms.)
E5	4	4	1.7415	1.7415
E6	2	6	1.8268	3.5683
E7	2½	8½	3.6440	7.2123
E8	3	11½	2.9573	10.1696
E10	3½	15	3.6116	13.7812
E11	2	17	3.7661	17. 5473
E12	2½	19½	3.9059	21.4532
E13	3	22½	3.8222	25.2754
J1	4	4	1.7921	1.7921
J2	4	8	3.3704	5.1625
J3	4	12	5.4116	10.5741
J4	8	20	11.7424	22.3165
J5	4	24	6.0421	28.3586
J6	4	28	6.1173	34.4759
J7	4	32	6.0011	40.4770
J8	4	36	6.2175	46.6945
J9	4	40	6.1834	52.8779
J10	8	48	9.0727	61.9516
J11	4	52	6.0989	68.0505
J12	4	56	6.1133	74.1618
J13	4	60	6.1072	80.2690
J14	4	64	6.0837	86.3527
J15	4	68	6.0013	92.3540

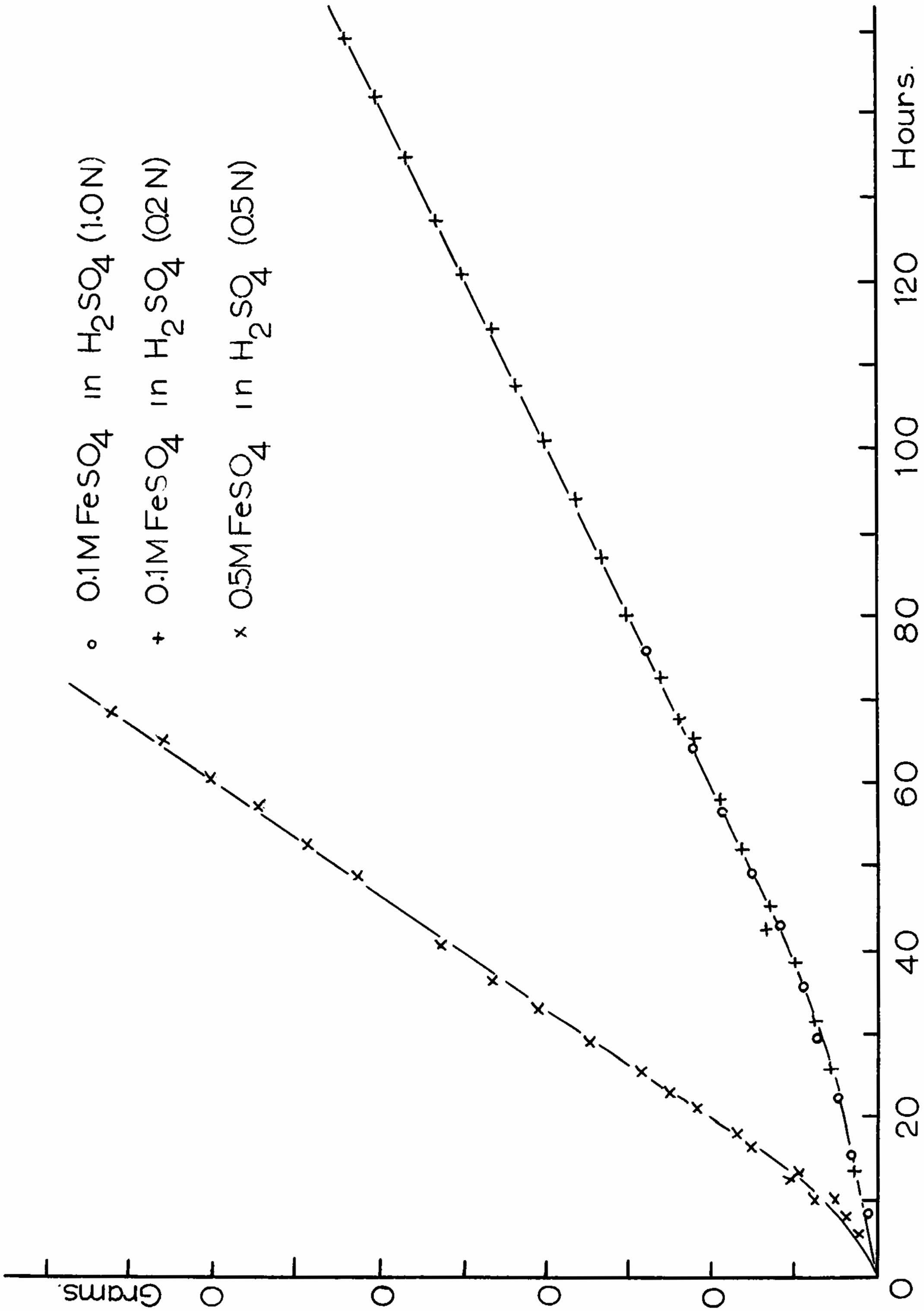


FIG 13

Yields of silver

Table X

Yields of Gold with solutions of $FeCl_3$ in HCl

Run No.	Duration (days)	Yield (gms.)	Conc. $FeCl_3$ (M)	Conc. HCL (N)	Conc. K_2CrO_4 (gm./l)	Rate of Prod. (gms./day)
F11	4	0.2554	0.2	1.0	½	0.064
F12	2	0.1900	0.2	1.0	½	0.095
F13	4	0.4997	0.2	1.0	1	0.125
F14	4	0.1109	0.2	1.0	¼	0.028
F15	4	0.3435	0.2	2.0	½	0.086
F16	4	0.1927	0.2	0.5	½	0.049
F17	4	0.3413	0.4	1.0	½	0.085
F18	4	0.1906	0.1	1.0	½	0.048

metals.

Fig. 10 and Table III show the effect of acid concentration on the yield of copper when sulphuric acid alone was the circulating liquid. Fig. 12 and Table V show the effect of varying the acidity with the cupric sulphate concentration kept constant at 0.5 mols per litre and also the effect of varying the cupric ion content when the acid concentration was kept at 0.5N.

The effects of variation of reagent concentrations in the case of silver may be seen directly on the yield curve, Fig. 13 and in Tables VII, VIII and IX. Table X shows this effect for gold.

Size Distribution of Crystals. The size distribution of copper crystals obtained with various circulating liquids is outlined in Table XI. These size distributions were obtained by the counting technique described above. Table XII lists the size distribution obtained with silver particles. This distribution was obtained by a seive analysis.

Tests were run to determine whether the duration of the run had any effect on the size distribution of copper crystals obtained. Tests were run with 0.5N sulphuric acid and 0.5M cupric sulphate in 0.5N sulphuric acid as circulating liquids. The results of these tests are listed in Table XIII. Similar tests were not carried out with silver and gold.

When the thread technique was used it was noted in all cases that the larger crystals grew on the upper, hotter portions of the thread and the smaller crystals on the lower, cooler sections. This was observed in the cases of all three metals. No quantitative determinations were made on these.

Shape Distribution of Copper Crystals. Shape distributions were determined for the copper crystals by a counting technique. Table XIV

Table XI

Size Distribution of Copper Crystals

Run No.	Circulant	% 0-99 ($x10^{-4}$ mm^2)	% 100-499 ($x10^{-4}$ mm^2)	% 500-999 ($x10^{-4}$ mm^2)
A1	0.5N H_2SO_4	88	7	½
A3	1.0N H_2SO_4	88	10	½
A4	3.1N H_2SO_4	89	10	½
A8	0.5M $CuSO_4$	95	4	½
C7	0.5M $CuSO_4$ 0.5N H_2SO_4	94	5	0
C8	0.5M $CuSO_4$ 1N H_2SO_4	95	5	0
B7	0.5M $CuSO_4$ 3N H_2SO_4	92	7	0
A9	0.05M $CuSO_4$ 0.5N H_2SO_4	95	4	½
B8	0.12M $CuSO_4$ 0.5N H_2SO_4	91	8	0
C9	0.25M $CuSO_4$ 0.5N H_2SO_4	95	4	½
C7	0.5M $CuSO_4$ 0.5N H_2SO_4	94	5	0
C2	0.5M Na_2SO_4 0.5N H_2SO_4	92	7½	½
C4	0.5M $ZnSO_4$ 0.5N H_2SO_4	93	5	1
A6	0.5M $Al_2(SO_4)_3$ 0.5N H_2SO_4	94	5½	0
B6	0.5M $Fe_2(SO_4)_3$ 0.5N H_2SO_4	91	9	0
C5	0.5M $CoSO_4$ 0.5N H_2SO_4	97	2	0

Table XI (con't)

Run No.	Circulant	% 0-99 ($x10^{-4}$ mm^2)	% 100-499 ($x10^{-4}$ mm^2)	% 500-599 ($x10^{-4}$ mm^2)
B3	0.5M $(NH_4)_2SO_4$ 0.5N H_2SO_4	84	14½	0
B4	0.5M $MnSO_4$ 0.5N H_2SO_4	86	13	½
A5	0.5M $MgSO_4$ 0.5N H_2SO_4	88	11	½
C6	0.1M $Ce(SO_4)_2$ 0.5N H_2SO_4	92	7	0
A7	0.5M $CdSO_4$ 0.5N H_2SO_4	87	12	0
C3	0.5M K_2SO_4 0.5N H_2SO_4	78	20	1
B5	0.5M $FeSO_4$ 0.5N H_2SO_4	81	16	1

Table XII

Size Distribution of Silver Particles

Circulant	$0.5M\ FeSO_4$ in $0.5N\ H_2SO_4$		$0.1M\ FeSO_4$ in $0.2N\ H_2SO_4$			
Run No.	E5	E8	E9	E17	E23	E24
Duration (hrs.)	3	3	4½	3	13½	13½
% + 100	0.9	0.7	4.5	0.9	2.0	6.9
% + 150	1.1	0.8	1.8	1.8	6.4	20.7
% + 200	3.7	4.6	6.5	5.3	8.4	26.2
% - 200	94.3	93.9	90.6	92.0	83.2	46.2

Table XIII

Effect of Duration of Run on Size Distribution of Copper Crystals

(a) Run No. B13 - 0.5N sulphuric acid circulating.

Time (hrs.)	0-99 (%) $(\times 10^{-4}\ mm^2)$	100-499 (%) $(\times 10^{-4}\ mm^2)$
12	89	11
48	87	10
72	90	9

(b) Run No. A11 - 0.5M cupric sulphate in 0.5N sulphuric acid circulating.

Time (hrs.)	0-99 (%) $(\times 10^{-4}\ mm^2)$	100-499 (%) $(\times 10^{-4}\ mm^2)$
12	97	3
24	96	4
48	96	3
78	96	4
96	97	2

shows the distribution obtained with various circulating liquids. Table XV shows the effect of varying the cupric ion concentration at constant acidity and Table XVI the effect of varying the acidity with a constant cupric ion concentration. Table XVII shows the effect which the duration of the run had on the shape distribution.

The Effect of Temperature. The thread technique described above was used to investigate the effect of temperature on the habits of the crystals obtained. A plot of the reciprocal of the temperature drop across a thread section against the average temperature of the section was made for the first appearance of each type of crystal found. The reciprocal of the temperature drop was chosen for the reasons outlined below in the discussion. The first appearance of a form was chosen as significant as it was thought that the appearance of the form below its place of first appearance could be accidental. There is the possibility that the crystal had been formed in an upper section of the cooling tube and had fallen through a portion of the tube before adhering to the thread.

Tables XIX to XLVIII in Appendix A summarize the experimental results obtained. Figs. 27 to 56 in Appendix B give the graphical results of these data. Figs. 14, 15 and 16 are composites of these individual graphs. These have been drawn without points being plotted in order to keep the graphs from becoming cluttered. They represent the conditions under which each habit was observed.

Figs. 17 to 20 are photographs of the crystals found with all three metals. The scale of magnification is indicated on each figure.

Table XIV

Shape Distribution of Copper Particles

Run No.	Circulant	% rods, needles, wires	% triangles	% stars	% hexagons	% irregular
A11	0.5M $CuSO_4$ 0.5N H_2SO_4	45.4	14.5	0.9	2.8	31.2
C8	0.5M $CuSO_4$ 1.0N H_2SO_4	49.7	14.9	3.5	5.3	21.0
B7	0.5M $CuSO_4$ 3.0N H_2SO_4	26.1	8.5	0.0	8.4	48.5
A9	0.05M $CuSO_4$ 0.5N H_2SO_4	36.2	7.2	0.0	5.2	45.5
B8	0.12M $CuSO_4$ 0.5N H_2SO_4	28.2	11.8	0.3	16.8	44.1
C9	0.25M $CuSO_4$ 0.5N H_2SO_4	35.7	12.4	0.3	8.1	38.2
C7	0.5M $CuSO_4$ 0.5N H_2SO_4	45.4	14.5	0.9	2.8	31.2
B5	0.5M $FeSO_4$ 0.5N H_2SO_4	2.8	----	---	47.5	46.2
B13	0.5N H_2SO_4	22.7	11.3	7.2	19.3	37.4

Table XV

Effect of Cupric Ion Concentration on Shape Distribution of Copper Crystals

(H_2SO_4 concentration constant at 0.5N)

Run No.	B13	A9	B8	C9	A11
Duration (hrs.)	24			45	12
$CuSO_4$ conc.	0.0M	0.05M	0.12M	0.25M	0.50M
% Rods	17.9	23.8	14.7	11.8	17.0
% Needles	3.8	5.9	9.7	11.8	13.5
% Bent Wires	1.0	6.5	3.8	12.1	13.2
% Triangles	11.3	7.2	11.8	12.4	14.5
% Squares	0.6	3.2	2.9	6.7	4.1
% Diamonds	0.7	2.6	0.0	1.3	0.3
% Hexagons	19.3	5.2	16.0	8.1	2.8
% Stars	7.2	0.0	0.3	0.3	0.9
% Dendrites	0.7	0.0	0.3	0.0	0.6
% Irregular	37.4	45.5	44.1	38.2	31.2
% Trapezoids	0.3	0.0	0.3	0.0	0.9
% Pentagons	0.0	0.0	0.0	0.0	0.6

Table XVI

Effect of Acidity on Shape Distribution on Copper Crystals

($CuSO_4$ concentration constant at 0.5M)

Run No.	A11	C8	B7
Duration (hrs.)	12	48	28
Acid conc.	0.5N	1.0N	3.0N
% Rods	17.0	31.6	13.1
% Needles	13.5	12.6	12.5
% Bent Wires	14.5	7.2	8.5
% Squares	4.1	3.2	3.0
% Diamonds	0.3	2.6	0.0
% Hexagons	2.8	5.2	8.4
% Stars	0.9	3.5	0.0
% Dendrites	0.6	0.0	0.6
% Irregular	31.2	21.0	48.5
% Trapezoids	0.9	0.0	0.0
% Octagons	0.0	0.3	0.0
% Pentagons	0.6	0.0	0.0

Table XVII

Effect of Duration of Run on Shape Distribution of Copper Crystals

B13			Run No.	A11		
$0.5N\ H_2SO_4$			Circulant	$0.5M\ CuSO_4$ in $0.5N\ H_2SO_4$		
24	48	72	Duration (hrs.)	12	48	96
17.9	13.1	16.1	% Rods	17.0	33.4	31.6
1.0	3.8	0.3	% Bent Wires	13.2	3.5	0.8
3.8	11.5	17.1	% Needles	13.5	8.5	3.4
11.3	14.1	19.8	% Triangles	14.5	12.0	18.6
0.6	0.0	5.7	% Squares	4.1	2.8	2.3
0.7	0.0	0.9	% Diamonds	0.3	0.0	0.0
19.3	18.0	21.6	% Hexagons	2.8	5.9	3.7
7.2	1.1	2.6	% Stars	0.9	0.3	3.4
0.7	0.0	0.6	% Dendrites	0.6	0.7	1.2
37.4	32.2	15.7	% Irregular	31.2	32.4	31.7
0.3	4.9	4.5	% Trapezoids	0.9	1.1	0.0
0.0	0.0	0.3	% Octagons	0.0	0.0	0.0
0.0	0.0	2.3	% Pentagons	0.6	0.0	0.5

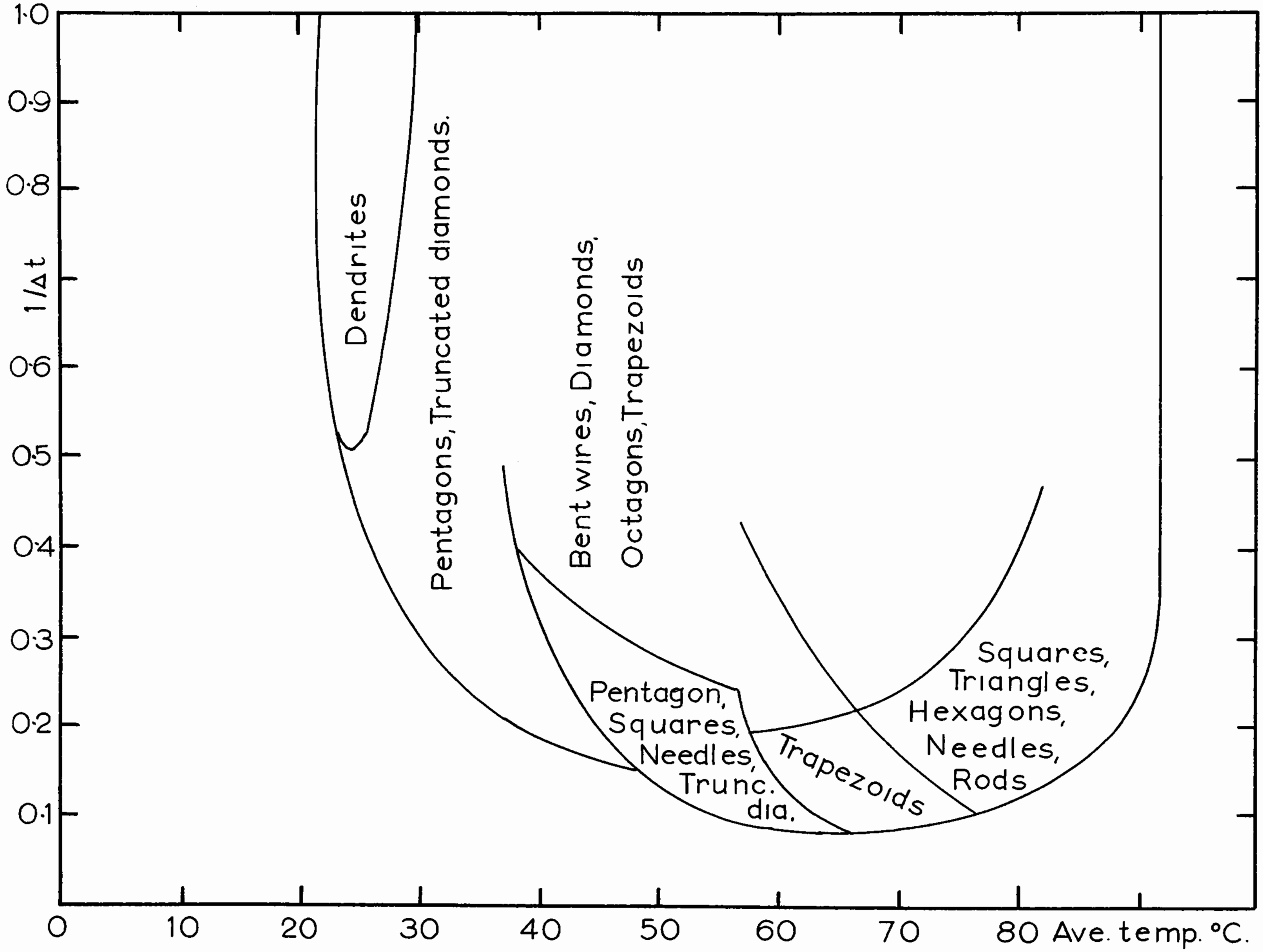


FIG. 14

Copper. Conditions for first appearance of various habits.

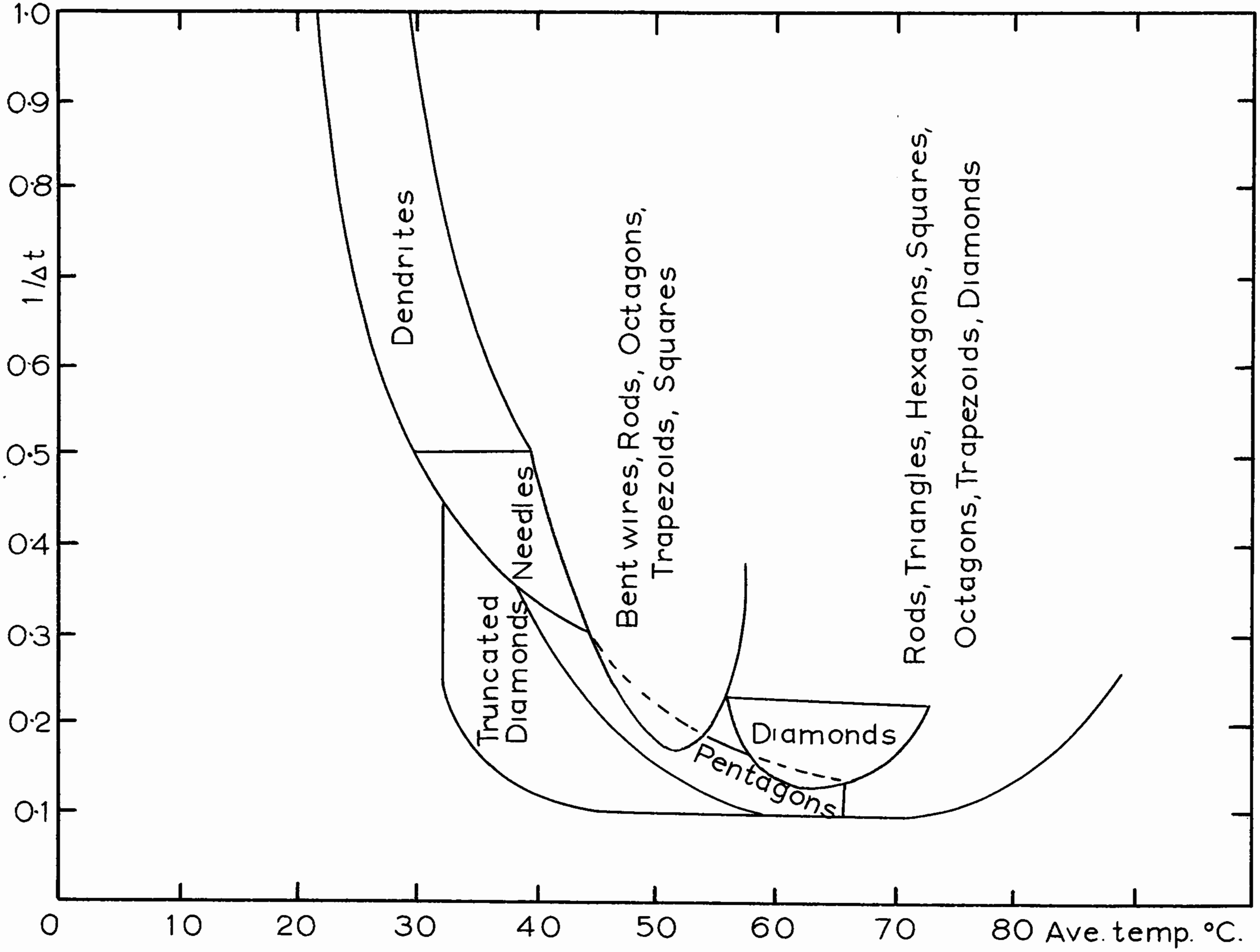


FIG. 15

Silver. Conditions for first appearance of various habits.

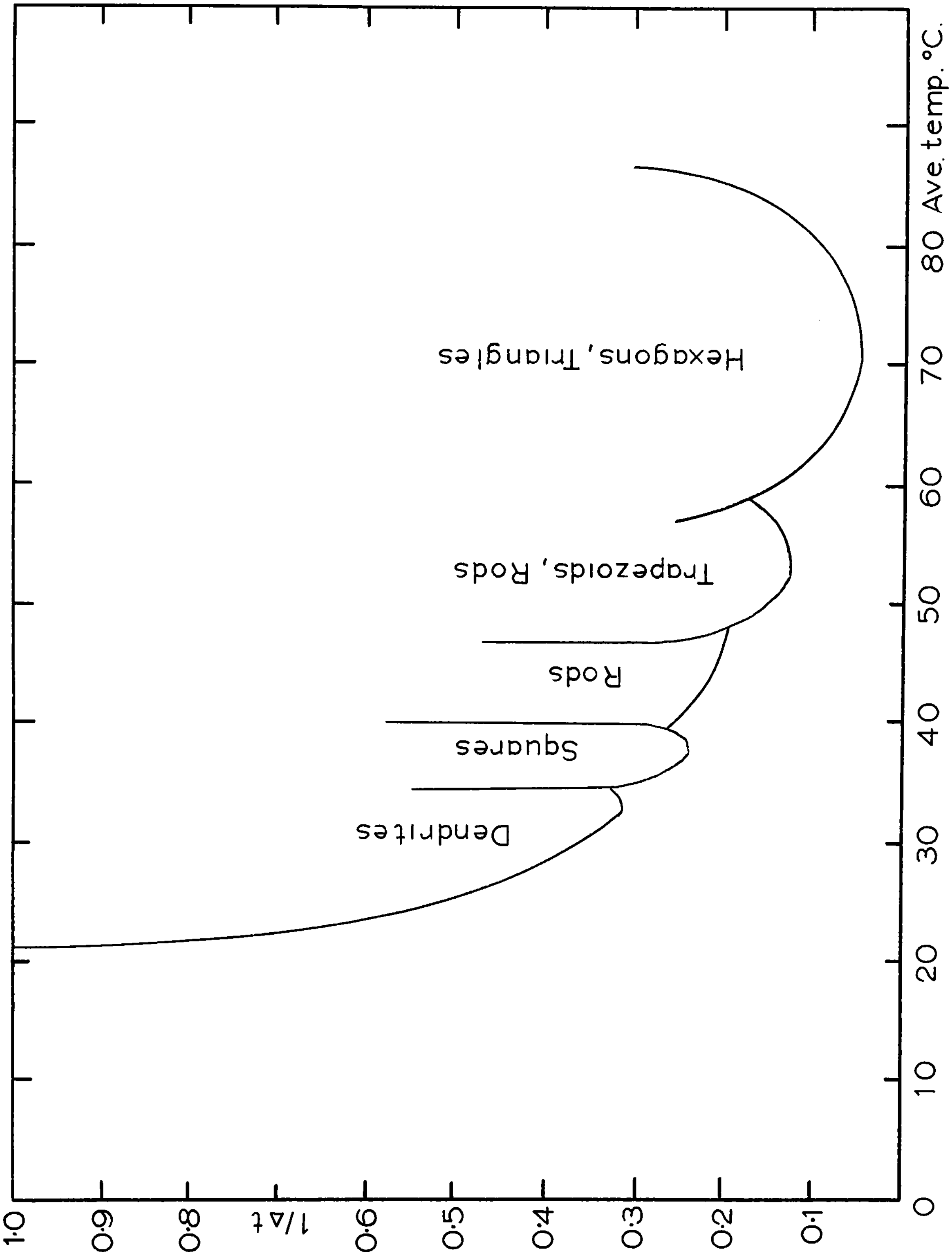
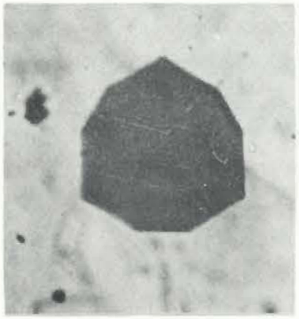


FIG 16

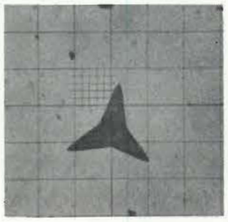
Gold. Conditions for first appearance of various habits.



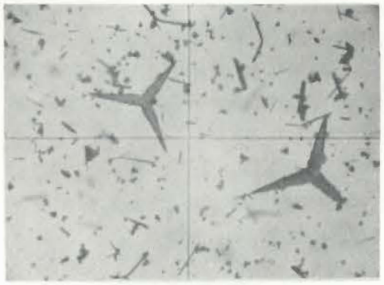
Gold (x 300)

Copper (x 600)

Copper (x 600)



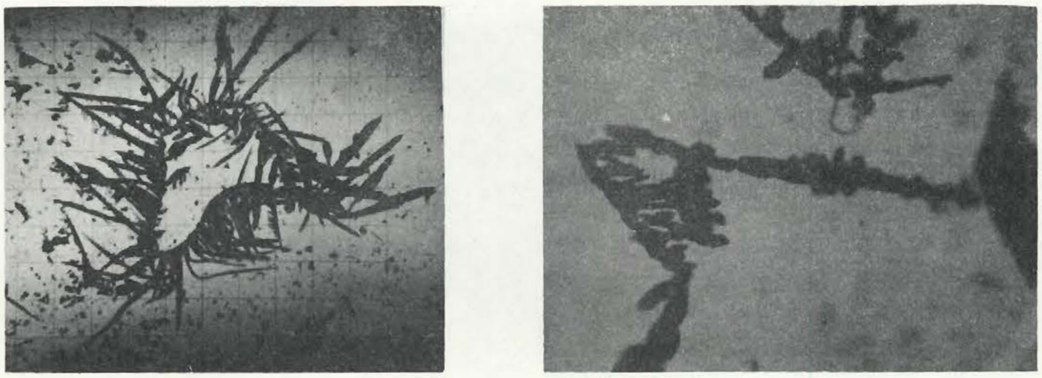
Copper (x 600)



Copper (x 360)

FIG. 17

Habits Observed on Few Occasions.



Copper

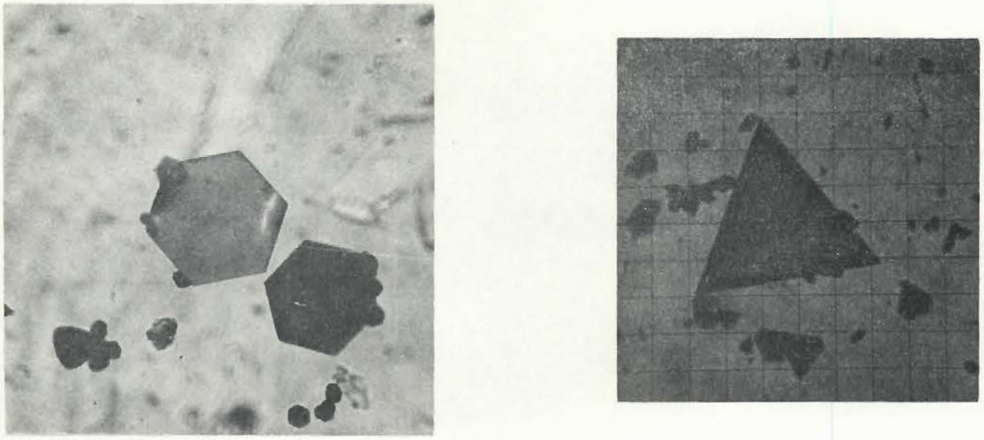
Silver

Gold

Copper

FIG.18

Dendrites

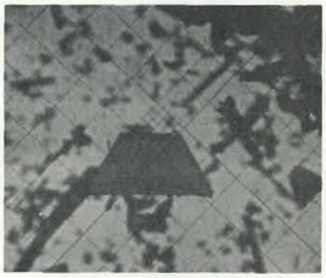


Hexagons

Triangles

Squares

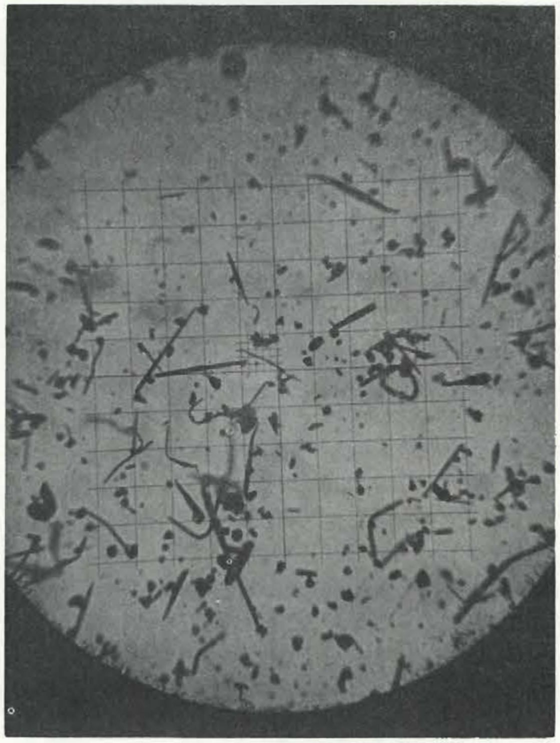
Rods



Trapezoids

FIG. 19

Regular Forms of Crystals Observed Consistently



Needles and Bent wires

FIG. 20

Irregular Forms of Crystals Observed Consistently

DISCUSSION OF RESULTS

Yields. Table III shows how the rate of production of copper crystals varies with the duration of the run using 0.5N sulphuric acid as the circulating liquid (Run B13). Fig. 10 shows the result graphically. As the duration of the run increases, the rate of production also increases. This is attributed to the attack of the copper wire by the sulphuric acid to form a solution of cupric sulphate. With an increase in time the amount of attack on the wire increases and the solution becomes more concentrated in cupric sulphate. The increased concentration of cupric ion increases the extent of the reaction

$$Cu^{++} + Cu \rightleftharpoons 2\ Cu^{+}$$

in the reaction flask so that on cooling more copper crystals are produced.

Table III and Fig. 10 also show the effect of changing the acid concentration on the yield. For an accurate comparison the same rates of flow should be used in all sets of apparatus. This is difficult to do with different solutions. The rate of flow is governed by the density of the solution and the temperature differential between the heating and cooling tubes. Runs with the same temperature differential do not necessarily have the same rates of flow because of the density factor. Since the duration of the run affects the composition of the circulating liquid, as shown above, comparisons should be made for approximately the same periods of time.

Fig. 10 shows that the yield of copper crystals is essentially independent of the acid concentration. The data in Table III show some slight deviations for comparable conditions, but these are not regarded as significant. The result is rather surprising; it would be thought that the stronger solutions of acid would attack the copper wire more quickly and result in solutions of cupric sulphate which were stronger. The yield of copper is obtained by the action of cupric sulphate on the copper wire and this yield is independent of the acidity, hence the cupric sulphate concentration is independent of the acidity when the reaction time is kept constant.

A survey of the literature on the mechanism of the reaction between sulphuric acid and copper was made in an attempt to find an explanation for the above observation. The survey showed that there was general agreement on the production of cupric sulphate as a product but there was disagreement about other products which were formed.

Davy (26) reported the formation of cupric sulphide. Pickering (78) found cuprous sulphide as well with the amount increasing up to 100°C and then decreasing as the temperature increased. Causse (21) noted the presence of cupric sulphite. Cundall (23) reported the formation of cuprous sulphate and suggested that two primary processes occurred, one at low temperatures and the other at high temperatures. Traube (93) detected the presence of hydrogen peroxide when dilute acid was used and reported that the presence of air was also necessary for reaction to occur. Rogers (83) suggested still another mechanism.

This last suggestion was made in 1926. In view of the discrepancies noted above it might be worth while to reinvestigate the mechanism of this reaction particularly determining the effect of the acid strength on the reaction. If different reactions occur with different acid concentrations this could account for the observations.

Another explanation could be postulated on the basis of relative rates of reaction. If the reaction between copper and sulphuric acid is slow compared to the formation and disproportionation of the cuprous ion, the rate of formation of crystalline copper could appear as independent of the acid concentration. No data are available to enable a decision to be made.

The solutions of sulphuric acid used as circulating liquids were analysed for cupric ion content after the runs had been completed. The results showed that with a given concentration the concentration of cupric ion increased with increasing time. When the concentration of acid was varied the cupric ion content increased slightly with increasing acid concentration. The cupric ion content increased approximately by a factor of 1.1 when the acid concentration was doubled. This seems to be a small increase for a large change in the acidity. Since the system used in this work was a dynamic one comparisons are not too meaningful unless the rates of circulation of the liquids were identical. These observations indicate that the experimental results above might possibly be due to the reaction mechanism.

Fig. 12 and Table V show the effects of the duration of the run on yields of copper crystals with solutions of cupric sulphate in sulphuric acid circulating. Fig. 10 shows that the rate of production is, in general, independent of the duration of the run.

Fig. 12 shows that when 0.5M copper sulphate without acid present was circulated over copper wire the production of copper crystals ceased after 2 days. Fig. 11 shows that the production ceased after about 7 days when 0.1M copper sulphate in 0.1N sulphuric acid was circulating. In both of these runs the wire in the reaction flask took on a red colour as the production of crystalline copper ceased. If this wire was now exposed to the air the red colour gradually became violet and then black. If the copper powder produced in the apparatus was not thoroughly washed it underwent the same colour changes. This coating on the copper is some oxidation product which is removed by the acid. If the wire was left in the reaction flask after the production of copper crystals had ceased, with the liquid still circulating, the wire became coated with a green salt and a green precipitate was found in the bottom of the reaction flask. This was presumed to be a basic copper sulphate as it dissolved in sulphuric acid. In the run using 0.1M copper sulphate in 0.1N sulphuric acid as the circulating liquid the pH of the solution changed from 1.62 to 2.62 from the start to the end of the run. This circulating liquid was used again with fresh copper wire and no copper crystals were formed after 48 hours of operation and the fresh wire had become coated with the red-violet oxidation product.

Two runs were made using cupric acetate dissolved in acetic acid as the circulating liquid. This combination was chosen to obtain a non-oxidizing acid whose cupric salt was soluble. The result was the same as observed above; no copper crystals were formed and the copper wire became coated with the same oxidation products.

From this it appears that the presence of an oxidizing acid and not just the presence of hydrogen ion is necessary to prevent the formation of these oxidation products on the metallic copper and to allow the formation of crystalline copper to continue.

Fig. 12 shows that the acid concentration in solutions of cupric sulphate has little effect on the yield of copper. However, with no acid present the yield is greatly reduced. The same figure shows the effect of varying the cupric ion concentration while keeping the acid concentration constant. It shows the expected result that the rate of production increases with an increasing concentration of cupric ion. The higher this concentration is, the greater is the concentration of cuprous ion in equilibrium with it. The copper powder is formed from the cuprous ion hence its amount will also be greater.

Doubling the cupric ion content resulted in the rate of production being increased by a factor of about 1.4. This factor can be attributed to the equilibrium involved. For the reaction

$$Cu + Cu^{++} \rightleftharpoons 2\ Cu^{+}$$

the equilibrium constant, K, is given as

$$K = [Cu^{+}]^2/[Cu^{++}] .$$

If the cupric ion concentration is doubled, the cuprous ion concentration must increase by $\sqrt{2}$ or 1.4 for the ratio to remain constant. Since the metallic copper produced is dependent on the cuprous ion content it should change by the same factor.

Table VI presents the results obtained when 0.5 molar solutions of various sulphate salts in 0.5N sulphuric acid were circulated over copper wire. These runs were primarily undertaken to determine if the presence of these salts had a modifying influence on the habit of the crystalline copper obtained. In most cases it can be seen that the rate of production of crystalline copper is slightly lower than when 0.5M sulphuric acid is circulating. Exceptions are noted in the cases of ferric and cupric sulphate and also in the case of ceric sulphate. It should be noted that in this case the concentration of the salt is 0.1 molar due to solubility limitations. The increased rate of production with these three salts is due to the fact that all three of these can act reversibly as oxidizing agents to attack the metallic copper and form cupric ion. This can then act further on the copper wire to form crystals. No explanation is offered for the slightly reduced rates of production in the presence of other salts.

Fig. 13 shows the results of yields obtained when solutions of ferrous sulphate in sulphuric acid were circulated over silver wire. These curves show a slight curvature in contrast to the linear curves obtained with copper. This difference can be explained in terms of the chemical reaction which occurs. The attack on the silver wire is brought about by the ferric ion and the reaction which occurs is

$$Fe^{+++} + Ag \rightleftharpoons Fe^{++} + Ag^{+}.$$

The amount of ferric ion present in the circulating solution is small at the start so that the attack on the metallic silver is slight. When the reaction is reversed only a small amount of silver ion is reduced to metallic silver and precipitated. As the experiment progresses the amount of ferric ion in the circulating solution increases until it reaches its equilibrium value and from there on the rate of production of silver crystals is constant.

Unlike the case with copper the cumulative yield does not level off after a period of time. The silver wire does not become coated with oxidation products which require acid for their removal. The presence of the acid has no effect on the rate of production of crystals as can be seen from Fig. 13. Its presence is necessary to prevent the hydrolysis of the iron salts and their precipitation as hydroxides or hydrated oxides.

Doubling the concentration of ferrous sulphate in the circulating solution resulted in an increase in the rate of production of crystalline silver by a factor of 1.6. This factor is not as easily explained as the factor of 1.4 obtained with copper. It could be due to the mechanism of the reaction. It could also possibly be due to complexing of the ions in solution and thus changing their effective concentrations. No data were found to support either of the possibilities. This aspect was not investigated during the present work since it was felt to be beyond the scope of the original problem.

Table X shows the yield results obtained with gold. Solutions of ferric chloride in hydrochloric acid with small amounts of potassium chromate were the circulating liquids. The presence of the chromate was necessary to cause a reaction. The chromate reacted with chloride ion to form free chlorine which in turn attacked the gold to give a solution containing gold ions in the + 1 and + 3 oxidation states. The species present in this solution are complexes since the aurous and auric ions, as such, are not stable in solution. A nominal reaction between the solution and the gold wire may be written as

$$2\,Au + Au^{+++} \rightleftharpoons 3\,Au^{+}.$$

Changing the concentrations of the constituents of the circulating solution had different effects. Doubling the amount of potassium chromate resulted in a doubling of the rate of production of gold crystals. Doubling the amount of chromate will double the amount of free chlorine produced and this in turn will double the amount of gold in the circulating solution since this is formed by the action of the chlorine on the gold wire. Doubling the acidity or doubling the concentration of ferric chloride resulted in an increase in the rate of production of crystalline gold by a factor of 1.4. However, when a solution of ferric chloride in hydrochloric acid without potassium chromate present was circulated no gold crystals were obtained. The reaction or reactions which are occuring are undoubtedly quite complex in view of the possible species present in solution. The changes in the rate of production are possibly related to the reaction mechanism.

No extended runs were made to determine yields with the gold wire as the rates were small and also because it was desired to preserve the gold wire for experiments on habit modifications as these changes were the primary concern of this investigation.

Particle Size. Table XIII summarizes the results of an investigation of the effect of the duration of the run on particle size distribution of copper powder. Runs were made using 0.5N sulphuric acid and 0.5M copper sulphate in 0.5N sulphuric acid as circulating solutions. In both cases the particle size was found to be independent of the length of time for which the liquid was circulated. This table also shows that the presence of cupric ion results in a larger proportion of smaller size crystals.

Table XI shows the results of size distribution studies on crystals of copper obtained with various circulating solutions. The table shows that when sulphuric acid was circulated the particle size distribution was independent of the acid concentration. When solutions of cupric sulphate in sulphuric acid were used the particle size distribution was independent of the cupric ion concentration. A comparison of these two series of experiments shows that higher proportions of larger crystals were formed when acid only was the circulating liquid. In most cases when solutions of sulphate salts in sulphuric acid were circulated the particle size distributions were either similar to that obtained with acid alone circulating or to that obtained when solutions of cupric sulphate in sulphuric acid were circulated. The exceptions were when the salt was ammonium sulphate, potassium sulphate or ferrous sulphate. In these three cases there was a higher proportion of larger crystals.

The difference in size distribution obtained when sulphuric acid or cupric sulphate in sulphuric acid were circulated can be explained as follows: With acid only circulating there is a low concentration of cupric ion in solution and hence a smaller amount of cuprous ion in equilibrium with this. In solutions containing cupric ion there will be a larger amount of cuprous ion at equilibrium. When the reaction is reversed in the cooling section of the apparatus, crystalline copper is formed from the cuprous ion. With a low concentration of cuprous ion the degree of supersaturation for precipitation of copper is low and under these conditions the nucleation of new crystals occurs slowly and crystals tend to grow rather than nucleate. When the degree of supersaturation is high, nucleation is the preferred process so that the resulting crystals are smaller.

No explanation is offered for the effects of the presence of other sulphate salts on particle size distributions.

Table XII gives a summary of the results of particle size distribution for silver particles. This distribution was obtained by seive analysis. Agreement of the various results is good except for the last two columns. The discrepancies are not actually as poor as these results indicate. The metallic silver crystals formed during the reaction tended to form agglomerates which were not separated by the seiving process. The crystal agglomerates tended to make the silver crystals appear larger than they actually were.

The gold crystals showed a greater tendency to adhere than the silver crystals so that no particle size determinations were undertaken.

Using the thread technique it was observed that the larger crystals were found in the hotter sections of the cooling tube and the smaller ones in the cooler sections. This observation can be explained in terms of supersaturation. At high temperatures there is a low degree of supersaturation and as a result growth of crystals occurs in preference to the nucleation of new ones. At low temperatures the degree of supersaturation is high and these are the conditions under which the nucleation of new crystals takes place in preference to the growth of existing crystals.

This observation on the effect of temperature on crystal size parallels that of Brown (11) on the growth of selenium crystals by deposition from the vapour. He noticed that the largest crystals grew in the hottest section of the deposition tube and the smallest crystals in the coolest section.

An attempt was made to study the effect of a change of viscosity in the circulating liquid. A series of runs was made using 0.1M copper sulphate in 0.1N sulphuric acid using solutions of glycerol as the solvent. Solutions of 10%, 25%, 50% and 90% glycerol by volume were used. The colours of these solutions became increasingly greener as the concentration of glycerol increased. The 90% solution had the green colour characteristically associated with solutions of nickel salts and the colour became more intense when the solution was heated. Presumably the colour change is due to complex formation between the cupric ion and the glycerol but no data on this system are available in the literature. It seems unusual that the colour should become more intense on heating.

The particle sizes became smaller with increasing concentrations of glycerol. With 90% glycerol as solvent the particles of copper were so small that they did not settle out in the collectors but were carried through the apparatus with the circulating liquid. When this liquid was filtered with suction through a sintered glass funnel a large proportion of the crystals passed into the filtrate.

Shape Distributions. Tables XIV, XV, XVI, and XVII summarize the data on shape distribution of copper crystals as determined by counting. An examination of these tables brings out the following generalizations:

(a) Increasing cupric ion content with constant acidity results in an increase in the proportion of needles; the relative amounts of other forms vary irregularly.

(b) Increasing acidity with constant cupric ion content results in an increase in the proportion of hexagons; the relative amounts of other forms vary irregularly.

(c) With increasing duration of the run using 0.5N sulphuric acid the percentage of irregular forms decreases while the percentages of needles and triangles increase.

(d) With increasing duration of the run using 0.5M cupric sulphate in 0.5N sulphuric acid the percentages of bent wires and needles decrease.

(e) In the presence of ferric ion there is a large increase in the percentage of hexagons present.

It is felt that this last observation is the only significant one. Ferric ion appears to have a definite modifying effect as the proportion of hexagons was substantially increased. The other variations, which show few regularities are possibly due to temperature variations or to the presence of impurities, such as dust, which are removed as the run progresses.

When an apparatus was used for the first time the circulating liquid containing cupric ion took on a cloudy appearance as it first circulated and this gradually cleared. A run such as this certainly would be carried out with dust and glass particles from the construction of the apparatus present. This cloudiness did not appear with later runs unless the apparatus had been out of service for a considerable length of time. In view of this it is felt that impurities were not primarily responsible for the variations in the relative amounts of the different forms.

In the runs using glycerol as solvent no new forms were found. With 10% glycerol rods and needles were the predominant forms. With 25% glycerol needles predominated and with 50% glycerol squares were the most abundant forms. With 90% glycerol the crystals were so small that it was possible to determine the shapes of the largest crystals only and hence the predominant form is not known. Dendrites were not found under any of these conditions. Glycerol seems to promote the formation of squares, triangles and hexagons. Buckley (15) stated that increases in viscosity slow down concentration currents and growth then tends to occur by diffusion. The result of this is a tendency toward dendritic growth. The results obtained here do not agree.

During some preliminary investigations a solution of cupric chloride in hydrochloric acid was circulated over copper wire and cuprous chloride settled out in the collectors in large amounts. An examination of these crystals under the microscope showed them to be triangular in shape or three pointed stars. This raised the possibility that the triangular forms obtained might be overgrowths of copper on cuprous chloride crystals, the cuprous chloride having been formed from traces of impurities. To test this a run was made using 0.1M cupric sulphate in 0.1N sulphuric acid containing 1 gram per litre of sodium chloride as the circulating liquid. Both crystalline copper and cuprous chloride were formed and gathered in the collectors. A microscopic examination showed that the two products were easily distinguishable and there was no increase in the quantity of triangles formed. From this it was concluded that this triangle shape was not due to an overgrowth on cuprous chloride but inherent in the formation of copper crystals.

As work progressed it became apparent that the temperature at which crystals were nucleated and grown was an important factor in habit formation. Brown (11) in his work on the growth of selenium crystals from the vapour phase noted a variety of forms and suggested that these were influenced by the partial pressure of selenium vapour and the temperature gradient at the place of growth in the deposition tube.

Nakaya (72) observed the growth of snow crystals by the deposition of water vapour. The temperature at which crystals of a given form grew was plotted against the supersaturation of the vapour for all forms of crystals observed (See Fig. 7). Each type of crystal was found to be within a fairly well defined region on this plot. The temperature of crystal growth appeared to be a more important factor than the supersaturation in determining the crystal habit. On this graph, plates and needles are shown to be formed at high temperatures and dendrites at low temperatures. Marshall and Langleben (60) argued that the excess of the ambient vapour density over that in equilibrium with the crystal at its temperature of growth determined the crystal habit. Crystal habit changes result when this excess is large enough to overcome the inhibitions to growth at the sides and corners of a crystal. Mason (61) maintained that temperature of growth seemed to be a more important factor than supersaturation in the determination of crystal habit. The temperature boundaries of the region of formation for a given crystal form are sharp while the supersaturation boundaries are not. The supersaturation was reported to affect the growth rate of crystals and the development of secondary features on a crystal.

The thread technique described in the experimental section above was devised to investigate the effects of supersaturation and temperature of growth on crystals of copper, silver and gold grown by the chemical reactions described above. The average temperature of a thread section was taken as the temperature of crystal growth and the temperature drop across a thread section was taken as a function of the supersaturation.

Plots were made with the temperature drop across a thread section and average temperature of a section as parameters for each form of crystal observed. The results were roughly similar to those of Nakaya except that boundaries of the regions of growth for different crystal habits were not as sharply defined. This could be due to the fact that more experimental data were determined in this work than in that of Nakaya. The observation made by Nakaya that plates and needles appeared at high temperatures and dendrites at low temperatures was also seen here in the cases of all three metals - copper, silver and gold. The main difference between these graphs and that of Nakaya was that they were inverted with respect to each other.

An attempt was made to calculate the actual extent of supersaturation in the case of copper. It was assumed that the disproportionation of the cuprous ion was a rapid reaction and that equilibrium was attained in all sections of the thread. The van't Hoff isochore gives the relationship of the equilibrium constants (K_1 and K_2) at two temperatures T_1 and T_2 as

$$\log \frac{K_1}{K_2} = \frac{\triangle H}{2.3R}\left[\frac{T_1 - T_2}{T_1T_2}\right]$$

and in this reaction K is given by $[Cu^+]/[Cu^{++}]^{\frac{1}{2}}$, $\triangle$ H is the heat of reaction and R the gas constant. For a given thread section $T_1 - T_2$ becomes the temperature drop across the section, $\triangle$ t, and T_1T_2 becomes, approximately, the square of the average temperature of the section. The cupric ion concentration is large in comparison to the cuprous ion concentration and it remains essentially constant for a given thread section. Under these conditions the van't Hoff isochore reduces to

$$\log [Cu^+]_1/[Cu^+]_2 = \frac{\triangle H}{2.3R} \cdot \frac{\triangle t}{Tave^2}$$

The ratio $[Cu^+]_1/[Cu^+]_2$ then becomes the supersaturation ratio and it is independent of the cupric ion concentration.

The heat of reaction $\triangle$H and the gas constant are known; $\triangle$t and the average temperature were measured. From these it was possible to evaluate the supersaturation ratio. The necessary calculations were done and a plot of supersaturation ratio and average temperature as parameters was made for each crystal form observed. The results did not change appreciably from the curves using average temperature and temperature drop as parameters. The peaks at the higher temperatures were lowered slightly and those at the lower temperatures were raised slightly.

Similar calculations were not made for silver and gold as the data were either not available or, if they were, they were found to have inconsistent values.

Let us examine the possible ways in which supersaturation could vary with temperature difference during precipitation or crystallization. There are three possible types of solubility curves, assuming an increase in solubility with increasing temperature. There is the possibility that the solubility varies linearly with temperature (Fig. 21a); that the solubility is concave upward (Fig. 21b) and that it is concave downward (Fig. 21c).

Ostwald (77) suggested that a supersolubility curve existed in addition to the solubility curve. The region above the supersolubility curve was labile and the region between the two curves represented a metastable state. Miers and Isaac (67, 68) found some experimental confirmation for this and reported the supersolubility curves to be approximately parallel to the solubility curves. The dashed lines in Fig. 21 represent these supersolubility curves.

On all three diagrams the path of cooling a solution is represented by the line DEC. When the system reaches the point C on the supersolubility curve, precipitation occurs, the process being represented by the line BC. At the temperature t_1, BC represents the actual amount of supersaturation and the ratio AC/AB represents the supersaturation ratio.

In Fig. 21a, BC is constant so that the supersaturation is constant and independent of temperature but the supersaturation ratio decreases as the temperature increases. Fig. 21b shows that for this type of solubility curve the length BC increases with increasing temperature so that the supersaturation increases with increasing temperature. As with the first case the supersaturation ratio decreases with increasing temperature but at a slower rate. In Fig. 21c the length BC decreases and hence the supersaturation decreases with increasing temperature. As with the previous two types of curve the supersaturation ratio decreases

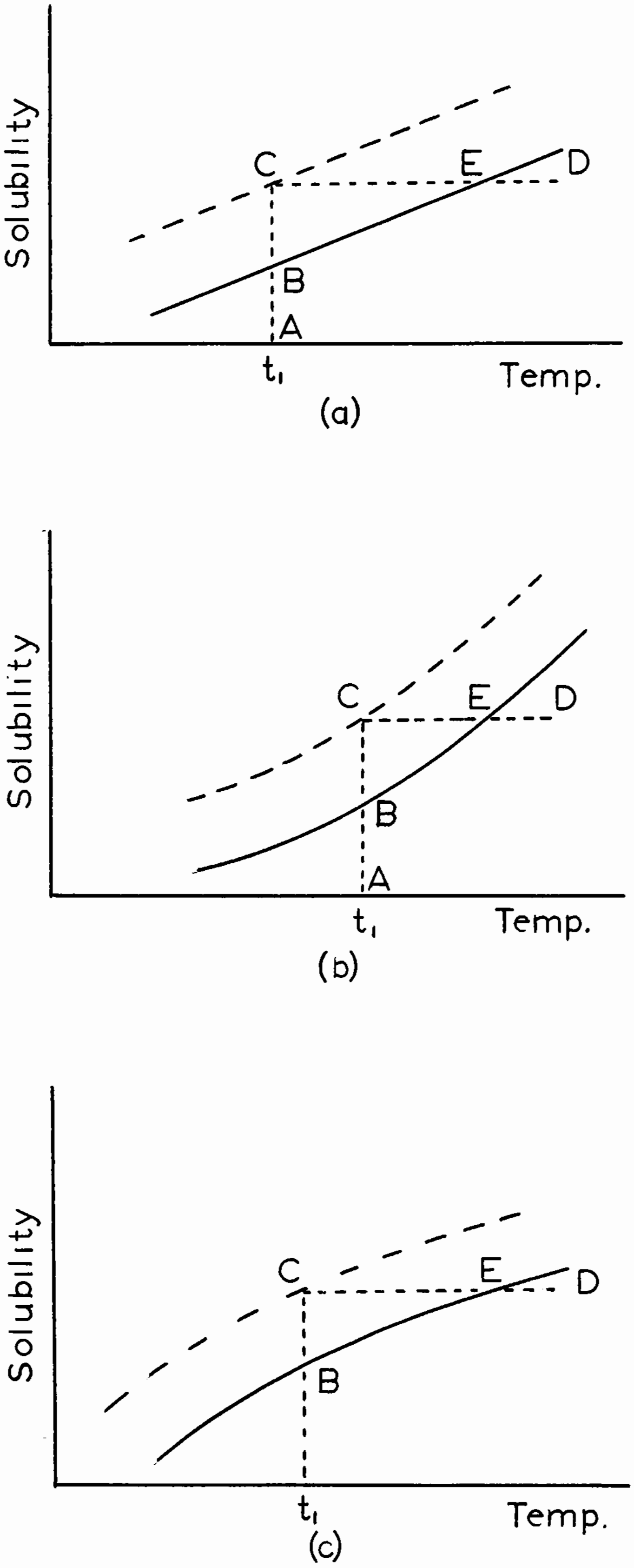


FIG. 21 Types of Solubility Curves

with increasing temperature but the rate of decrease is more rapid.

The distance EC represents the temperature drop associated with the crystallization. In Fig. 21a this line is constant in length and independent of the temperature. In Fig. 21b the length of EC decreases with increasing temperature and in Fig. 21c it increases with increasing temperature.

Fig. 21a represents a situation where the supersaturation and temperature drop associated with crystallization are constant, hence independent of the temperature. Fig. 21b represents a case where the supersaturation increases with increasing temperature while the temperature drop associated with crystallization decreases with increasing temperature. Fig. 21c represents conditions where the supersaturation decreases and the temperature drop associated with crystallization increases with increasing temperature. In these latter two cases the supersaturation and temperature drop are related inversely. Fig. 21b is a solubility curve where the solubility tends to an infinite amount at high temperature and Fig. 21c is one where the solubility tends to a maximum value which then remains unchanged with increases in temperature.

The cases discussed above assumed that the solubility of the solute increased with increasing temperature. A similar argument can be applied to solubility curves where a decrease in solubility occurs with increasing temperature and similar results will be obtained.

In view of the above demonstration that the supersolubility and temperature drop associated with crystallization may be related inversely and in view of the reversal of the temperature drop-average temperature curves by comparison with the results of Nakaya the experimental data were replotted with average temperature of a thread section and reciprocal of temperature drop across a thread section as parameters. Figs. 27 to 56 in Appendix B give the results which are summarized in Figs. 14, 15 and 16.

In general the results are similar to those of Nakaya. The results with gold divide the graph into relatively well defined areas for each form observed. With copper and silver there is some overlap of these growth regions. This could be due to the fact that fewer habits were observed with gold or due to an incorrect classification of the observed forms. Some of the forms classified as different may, in reality, not be so.

A comparison of Figs. 14, 15 and 16 brings out the following:

(a) On all curves the regions where dendrites, triangles, trapezoids and hexagons grow are in similar positions.

(b) The regions where rods occur are at high temperatures with copper, at intermediate temperatures with gold and at both high and intermediate temperatures with silver.

(c) Squares appear in different regions with all three metals.

(d) With copper and silver the bent wires and truncated diamonds occur in roughly the same positions.

(e) With copper and silver the regions where pentagons, diamonds, octagons and needles occur are quite different.

On the basis of the above figures it would be difficult to state that either the supersaturation or the temperature of growth was the more important factor in determining crystal habit. In the case of dendrites the temperature of growth is obviously the more important factor with all three metals. With gold, temperature of growth seems to be more important except for the growth of triangles, hexagons and rods where both temperature and supersaturation have an influence. With silver, temperature of growth seems to be more important for the growth of needles and bent wires. For other forms both factors seem important. The forms observed with copper seem to be dependent on both factors except for dendrites. Silver seems to be intermediate in its behaviour between copper and gold.

The only work which closely resembles that done in this investigation is the work of Courtney (22). He grew silver crystals on microscope slides by a reduction of silver ions with ferrous ions. He observed that triangular and hexagonal plates grew before needles. His work was primarily an investigation on the rate of growth of needles. His observation of triangles and hexagons agrees with the results obtained here but unfortunately Courtney reported no temperature data.

It should be possible to adapt the procedure used above to demonstrate the relationship between supersolubility and temperature drop to obtain qualitative solubility and supersolubility curves. A smooth curve joining all the minimum points on the $1/\Delta t$ vs average temperature curves for a given metal is drawn. This line gives the reciprocal of the temperature drop associated with precipitation at a given temperature. The reciprocal of the temperature drop in turn is related to the supersaturation. The data obtained with copper, silver and gold indicated that $1/\Delta t$, and hence the supersaturation, decreases with increasing temperature. This indicates that the solubility and supersolubility curves should be similar to that of Fig. 21c. The problem becomes one of drawing two parallel lines such that $1/\Delta t$ represents the difference between their ordinates. Fig. 22 illustrates the problem graphically. The upper curve is the supersolubility curve. AC is the

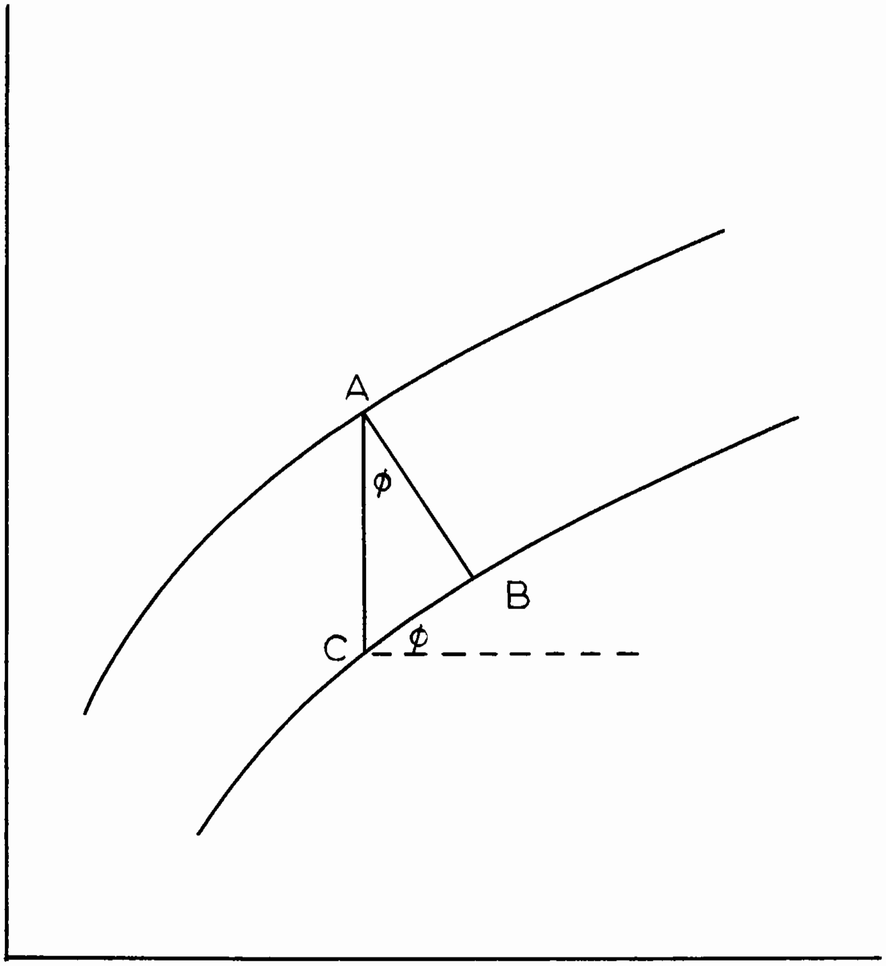


FIG. 22

Relationship Between Supersolubility and Solubility Curves supersaturation which is proportional to $1/\Delta t$ and AB is the distance between the parallel curves. At high temperatures, where $1/\Delta t$ is independent of the temperature, the two lines become horizontal and AB and AC become the same line. Assuming that ABC is a right angled triangle it is now possible to find the angle ϕ. It is the angle whose cosine is the ratio AB/AC and the values of these are known. Having found the value of ϕ the slope of the solubility curve at the point C is known and the supersolubility curve is parallel to this. By a repetition of this procedure at various temperatures the solubility and supersolubility curves can be qualitatively estimated.

Let us illustrate this with the data from the copper system. Table XVIII summarizes the data. The temperature, t, and the value of $1/\Delta t$ have been obtained from Fig. 14. Beyond 65°C the value of $1/\Delta t$ is constant so that the solubility and supersolubility curves are approximately horizontal from this temperature. The value of $1/\Delta t$ at 65°C is taken as a measure of AB in Fig. 23. The values of AB/AC are calculated as 0.080 divided by $1/\Delta t$. This allows the angle ϕ to be found.

A line is drawn from 22.5°C to 27.5°C at an angle of 81°. From 27.5°C to 32.5°C the line is continued at an angle of 74°. This procedure is continued until the solubility curve is estimated. The supersolubility curve is then drawn parallel to this separated by a distance representing 0.080 units. Fig. 23 gives the overall result. It must be remembered that this represents the solubility of copper in solutions of cupric sulphate in sulphuric acid. Figs. 24 and 25 are the corresponding curves for silver and gold.

It was not expected to observe the growth spirals associated with the dislocation theory of crystal growth under the experimental

Table XVIII

Data for Estimating Solubility Curve of Copper

t °C	$1/\Delta t$	$\cos \phi = 0.080/1/\Delta t$	ϕ
25	0.55	0.145	81°
30	0.30	0.266	74°
35	0.24	0.333	70°
40	0.19	0.421	65°
45	0.16	0.500	60°
50	0.13	0.615	52°
55	0.10	0.800	36°
60	0.082	0.965	15°
65	0.080	1.00	0°
70	0.080	1.00	0°
75	0.080	1.00	0°

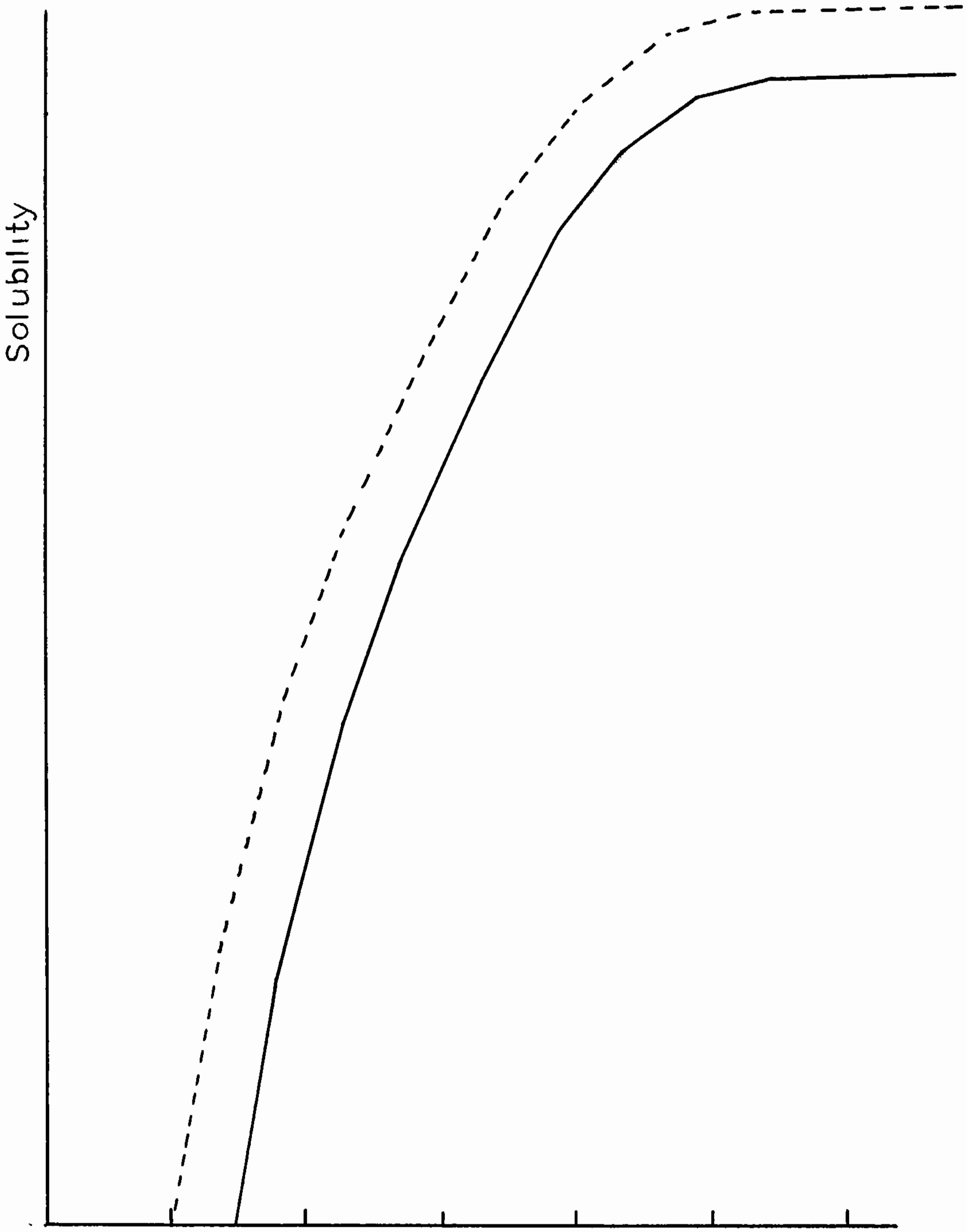


FIG. 23

Solubility and Supersolubility of Copper

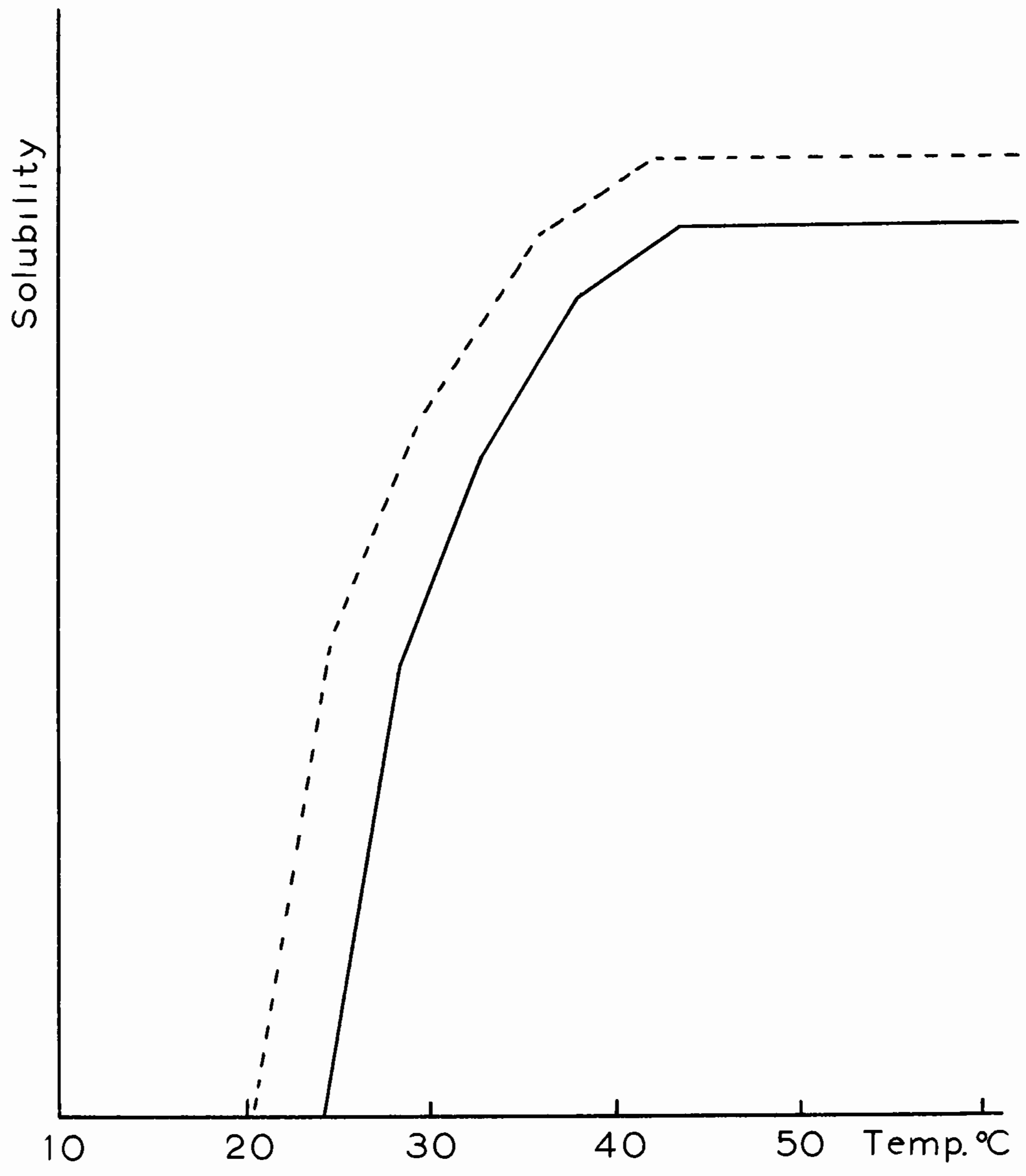


FIG. 24

Solubility and Supersolubility of Silver

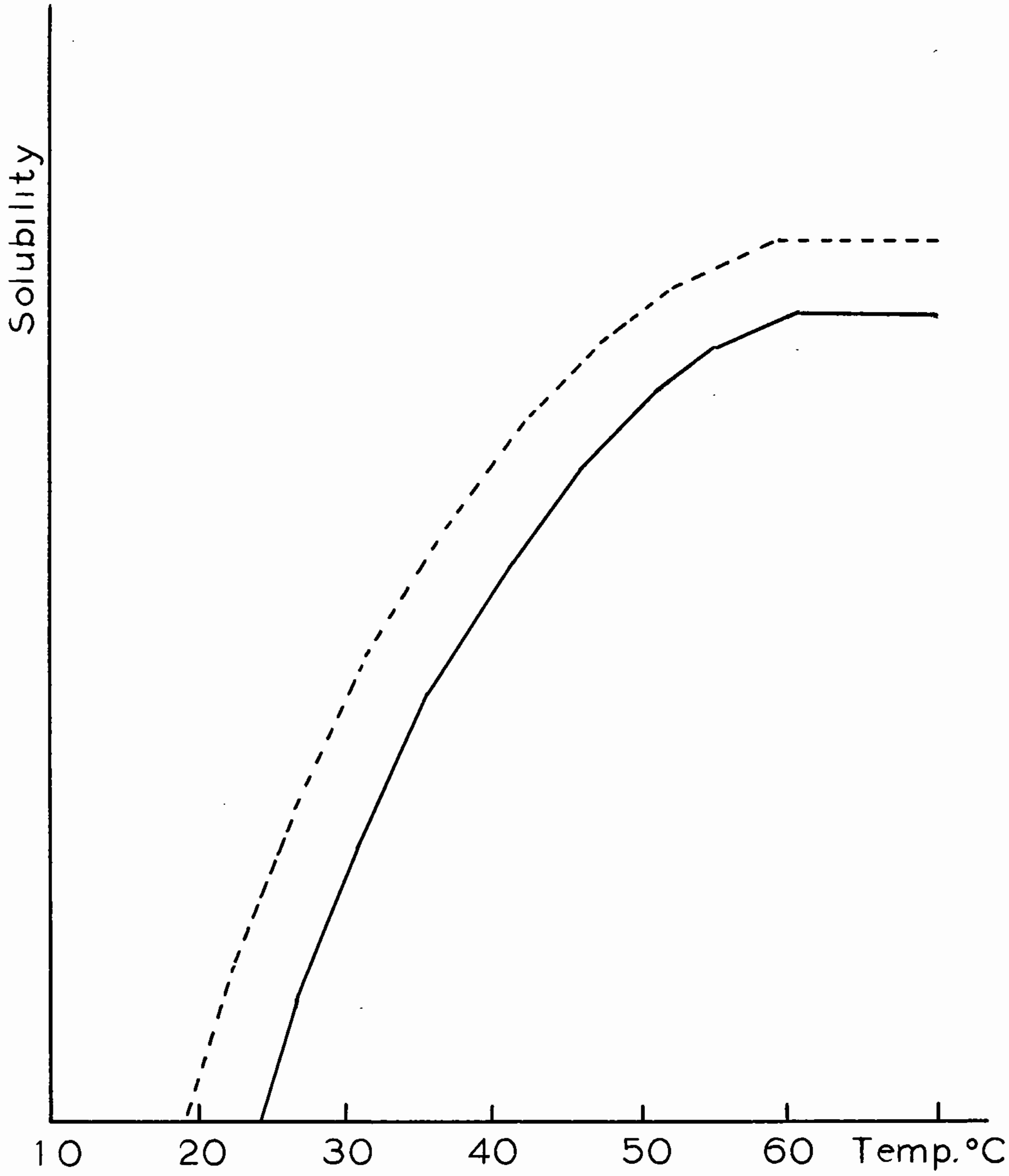


FIG. 25

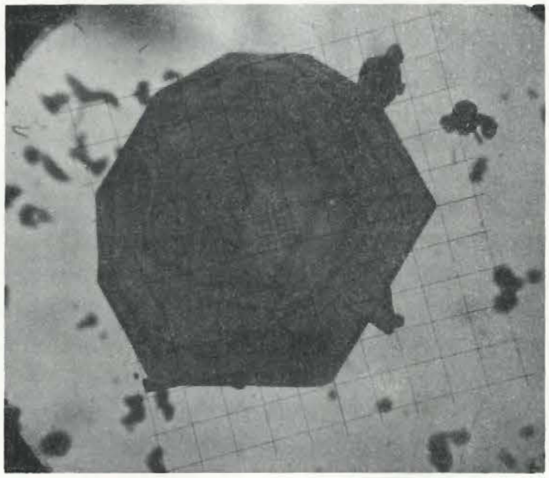
Solubility and Supersolubility of Gold.

conditions used since these occur in steps a few molecular diameters in height. Surface markings were observed on one occasion with copper and on many occasions with silver. These are illustrated in Fig. 26. The copper markings are definite steps, those on the crystals of silver were dendritic.

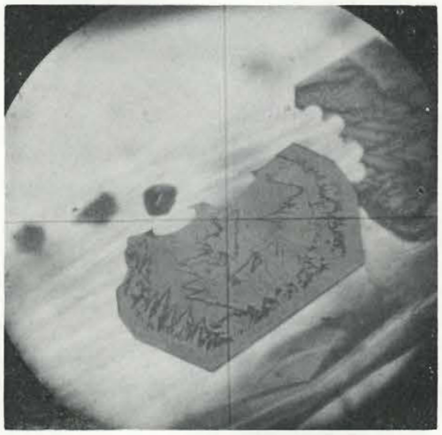
Copper crystals were observed on a number of occasions with needle-like extensions. With hexagons these extensions occurred along one side parallel to it or they extended from a corner parallel to the diameter which included this apex. Triangles showed extensions only along the side. Rods showed extensions parallel to the long side growing either as a continuation of the side or from the mid point of the short side. Extensions such as these were not observed on the silver and gold crystals.

In his work on the growth of mercury crystals from the vapour state Sears (85) attributed needle or whisker growth to a single screw dislocation at the tip of the whisker and plate growth to two screw dislocations at right angles. If the same applies to this work then in the case of copper, temperature of growth and supersaturation have no effect on the origin of these dislocations since plates and needles grow under the same conditions. This same result is seen with silver crystals. No observation can be made in the case of gold crystals since no needle crystals were found.

In general the results obtained here agree with the observation of Mokievski (70) that supersaturation has little effect on the shape of crystals grown under dynamic conditions. In agreement with the reported facts on crystal growth (see p. 30) the more regular crystals were grown at high temperatures and low supersaturations.



(a) Copper (x600)



(b) Silver (x360)

FIG. 26

Surface Markings on Crystals

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

Crystals of copper, silver and gold have been grown by reversible oxidation-reduction reactions in aqueous solution. Sulphuric acid was used as a circulating liquid over copper wire for the production of copper crystals. The yield of copper obtained and the rate of production of the crystals were found to be independent of the strength of the acid solutions. It is suggested that this result is due to the mechanism of the reaction. When solutions of cupric sulphate in sulphuric acid were circulated over copper for the production of copper crystals the rate of crystal production was found to be independent of the duration of the run. The rate of production increased with increasing cupric ion concentrations but was independent of the acid concentration. The presence of an acid capable of oxidizing action was found to be necessary to prevent the coating of the copper wire with oxidation products which caused the formation of crystalline copper to cease. A doubling of the cupric ion concentration resulted in an increase in the rate of production of copper crystals by a factor of 1.4. This has been explained in terms of the cuprous-cupric ion equilibrium. When solutions of other sulphate salts in sulphuric acid were used the rates of production were found to be approximately the same as when acid only was circulated unless the cation of the salt was capable of oxidizing action when the rate was increased. This has been explained as being due to the formation of an increased concentration of cupric ion in the circulating solutions under such conditions.

Yields of silver crystals obtained by circulating solutions of ferrous sulphate in sulphuric acid over silver wire were found to be independent of the acid concentration but dependent upon the concentration of ferrous ion. The presence of the acid is required to prevent the hydrolysis of the iron salts. Doubling the concentration of ferrous ion resulted in an increase in the rate of production of silver crystals by a factor of 1.6. The mechanism of the reaction is suggested as an explanation.

Solutions of ferric chloride in hydrochloric acid containing small amounts of potassium chromate were circulated over gold for the production of gold crystals. The yield was found to vary with the concentrations of all three materials. Doubling the potassium chromate concentration resulted in a doubling of the yield of gold crystals. Doubling the concentration of either the ferric chloride or hydrochloric acid resulted in an increase in the yield of gold by a factor of 1.4 An explanation is offered in terms of the chemical reactions.

Particle size distributions were determined for the copper crystals obtained. The size distribution was found to be independent of the duration of the run. When solutions of sulphuric acid were circulated the size distribution was found to be independent of the acidity. There was a higher proportion of larger crystals obtained with these solutions than with solutions of cupric sulphate in sulphuric acid. With solutions of cupric sulphate in sulphuric acid the particle size distribution was independent of the cupric ion concentration. These results were explained in terms of relative supersaturation.

Using the thread technique the larger crystals were found to grow in the hotter, upper portions of the cooling tube and the smaller crystals in the lower cooler sections. This has also been explained in terms of supersaturation. The presence of glycerol in the circulating solution caused a marked decrease in the particle sizes.

Shape distributions were determined for copper crystals by counting and no conclusive results were found for the causes in the shape changes. The presence of ferric ion was found to bring about a marked increase in the proportion of hexagonal plates present. The presence of glycerol had no modifying effect. An expected increase in the proportion of dendritic crystals with glycerol present was not confirmed. Triangular plates of copper were shown not to be due to overgrowths on crystals of cuprous chloride.

The reciprocal of the temperature drop across a thread section used for crystal growth has been shown to be related to supersaturation. A plot using average temperature of the thread section and reciprocal of temperature drop as parameters was prepared for each crystal form observed. It was found that with copper, silver and gold dendrites grew at low temperatures and triangular and hexagonal plates at high temperatures. In the growth of dendrites of all three metals the temperature of growth was found to be more important than supersaturation. In the crystal forms found with copper, other than dendrites, temperature of growth and supersaturation were both found to be important. With gold the temperature of growth, in most cases was found to be the important factor and the results obtained with silver were intermediate between those for copper and gold. Neither supersaturation nor temperature of growth appears to be the controlling factor for all types of crystal growth.

Qualitative solubility and supersolubility curves of the coinage metals in the solutions used have been obtained.

Surface markings were observed with copper and silver crystals.

Copper crystals were observed with needle like extensions. No explanation is offered for these observations.

APPENDIX A

Tabulated Experimental Data for Growth Regions

The circulating liquids used in these runs are indicated by the series letter of the runs. In the case of copper the circulating liquid was 0.1M copper sulphate in 0.1N sulphuric acid except in cases noted below, and the circulating liquid was 1.0M copper sulphate in 1N H_2SO_4 in series G. In the D series of runs the symbol (a) beside the run number indicates 0.5M copper sulphate in 0.5N sulphuric acid was circulated; the symbol (b) indicates 0.1M copper sulphate in 1N sulphuric acid was used; (c) indicates 0.1M copper sulphate in 2N sulphuric acid as the circulating liquid and (d) indicates 0.1M copper sulphate in 3N sulphuric acid was used.

In the data for silver 0.1M ferrous sulphate in 0.5N sulphuric acid was used in series E; 0.1M ferrous sulphate in 1N sulphuric acid in series H and 0.5M ferrous sulphate in 0.5N sulphuric acid in series J.

The circulating solutions used in the runs with gold were as follows: 0.2M ferric chloride in 1N hydrochloric acid with $\frac{1}{2}$ gram per litre of potassium chromate in runs F11 and F12; 0.2M ferric chloride in 1N hydrochloric acid with 1 gram per litre of potassium chromate in series F13; 0.2M ferric chloride in 1N hydrochloric acid with $\frac{1}{4}$ gram per litre of potassium chromate in series F14; 0.2M ferric chloride in 2N hydrochloric acid with $\frac{1}{2}$ gram per litre of potassium chromate in series F15; 0.2M ferric chloride in 0.5N hydrochloric acid with $\frac{1}{2}$ gram per litre of potassium chromate in series F16; 0.4M ferric chloride in 0.5N hydrochloric acid with $\frac{1}{2}$ gram per litre of potassium chromate in series F17 and 0.1M ferric chloride in 0.5N hydrochloric acid with $\frac{1}{2}$ gram per litre of potassium chromate in series F18.

Table XIX

Copper - conditions for first appearance of bent wires

Run No.	Outlet Temp $^{\circ}C$	Inlet Temp $^{\circ}C$	Ave. Temp $^{\circ}C$	Δ t C°	$1/\Delta$ t
D3	41	51	46	10	0.10
D4	26	30	28	4	0.25
D5	35	36	35.5	1	1.00
D6	26	27	26.5	1	1.00
D10	40	44	42	4	0.25
(a) D12	32	34	33	2	0.50
D13	38	41	39.5	3	0.33
D15	82	84	83	2	0.50
(a) D16	44	46	45	2	0.50
D17	67	72	69.5	5	0.20
D18	72	79	75.5	7	0.14
D19	49	55	52	6	0.17
D22	38	40	39	2	0.50
(d) D26	55	60	57.5	5	0.20
(c) D27	67	73	70	6	0.17
(b) D28	63	71	67	8	0.13
D29	62	67	64.5	5	0.20
D30	54	58	56	4	0.25
D31	50	53	51.5	3	0.33
D32	41	44	42.5	3	0.33
D35	56	61	58.5	5	0.20
D36	56	60	58	4	0.25
D37	44	48	46	4	0.25
D38	69	75	72	6	0.17

Table XIX con't

Run No.	Outlet Temp ^{o}C	Inlet Temp ^{o}C	Ave. Temp ^{o}C	Δt C^{o}	$1/\Delta t$
D39	50	52	51	2	0.50
D40	48	52	50	4	0.25
D41	51	57	54	6	0.17
D44	63	67	65	4	0.25
D45	61	67	64	6	0.17
D47	46	48	47	2	0.50
D49	58	64	61	6	0.17
D50	50	55	52.5	5	0.20
D52	49	53	51	4	0.25
D53	54	56	55	2	0.50
D54	48	52	50	4	0.25
D55	53	55	54	2	0.50
D56	37	43	40.5	7	0.14
D57	54	57	55.5	3	0.33
D58	65	70	67.5	5	0.20
D59	60	65	62.5	5	0.20
D60	63	69	66	6	0.17
D61	65	70	67.5	5	0.20
D62	62	68	65	6	0.17
D63	54	58	56	4	0.25
G1	48	54	51	6	0.17
G2	44	54	49	10	0.10
G3	56	62	59	6	0.17
G4	44	49	46.5	5	0.20
G5	55	60	57.5	5	0.20

Table XIX con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δ t C°	1/Δ t
G6	64	69	66.5	5	0.20
G7	40	43	41.5	3	0.33
G8	44	48	46	4	0.25
G9	32	35	33.5	3	0.33
G11	49	56	52.5	7	0.14
G14	50	57	53.5	7	0.14
G18	28	32	30	4	0.25

Table XX

Copper - conditions for first appearance of dendrites

Run No.	Outlet Temp ^oC	Inlet Temp ^oC	Ave. Temp ^oC	Δ t C^o	1/Δ t
D5	26	27	26.5	1	1.00
D6	26	27	26.5	1	1.00
(a) D9	22	23	22.5	1	1.00
(a) D12	22	22	22	0	
(a) D16	33	34	33.5	1	1.00
D18	27	28	27.5	1	1.00
D22	31	32	31.5	1	1.00
D29	26	27	26.5	1	1.00
D33	25	26	25.5	1	1.00
D34	29	29	29	0	
D35	29	30	29.5	1	1.00
D37	24	25	24.5	1	1.00
D38	31	31	31	0	
D41	27	28	27.5	1	1.00
D42	24	25	24.5	1	1.00
D45	30	31	30.5	1	1.00
D46	20	20	20	0	
D51	22	23	22.5	1	1.00
D52	25	26	25.5	1	1.00
D56	19	19	19	0	
D58	26	27	26.5	1	1.00
D59	21	21	21	0	
G5	24	25	24.5	1	1.00
G7	26	27	26.5	1	1.00

Table XX con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	△ t C°	1/△ t
G8	19	20	19.5	1	1.00
G9	31	32	31.5	1	1.00
G14	19	20	19.5	1	1.00
G15	19	20	19.5	1	1.00
G16	18	18	18	0	
G17	20	20	20	0	
G18	23	26	24.5	3	0.33

Table XXI

Copper - conditions for first appearance of diamonds

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	∆ t C°	1/∆ t
D3	4	4	4	0	
D5	35	36	35.5	1	1.00
D6	24	25	24.5	1	1.00
(a) D9	22	23	22.2	1	1.00
D10	34	37	35.5	3	0.33
(a) D12	36	38	37	2	0.50
D13	38	41	39.5	3	0.33
D15	66	71	68.5	5	0.20
(a) D16	46	49	47.5	3	0.33
D17	72	76	74	4	0.25
D18	61	67	64	6	0.17
D19	42	44	43	2	0.50
D22	31	33	32	2	0.50
(d) D26	60	65	62.5	5	0.20
(c) D27	39	41	40	2	0.50
(b) D28	35	37	36	2	0.50
D29	67	71	69	4	0.25
D30	62	65	63.5	3	0.33
D31	50	53	51.5	3	0.33
D32	56	61	58.5	5	0.20
D33	36	39	37.5	3	0.33
D35	44	48	46	4	0.25
D36	52	56	54	4	0.25
D38	65	69	67	4	0.25

Table XXI con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
D39	62	65	63.5	3	0.33
D40	39	41	40	2	0.50
D41	47	51	49	4	0.25
D42	65	70	67.5	5	0.20
D43	30	32	31	2	0.50
D47	44	46	45	2	0.50
D48	56	60	58	4	0.25
D49	58	64	61	6	0.17
D50	62	67	64.5	5	0.20
D51	56	60	58	4	0.25
D52	49	53	51	4	0.25
D53	47	49	48	2	0.50
D54	60	64	62	4	0.25
D56	35	37	36	2	0.50
D57	57	60	58.5	3	0.33
D61	47	51	49	4	0.25
D64	55	59	57	4	0.25
G5	45	49	47	4	0.25
G6	52	56	54	4	0.25
G7	30	32	31	2	0.50
G8	44	48	46	4	0.25
G9	30	31	30.5	1	1.00
G16	18	18	18	0	
G17	19	19	19	0	
G18	70	57	63	13	0.07

Table XXII

Copper - conditions for first appearance of hexagons

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δ t C°	1/Δ t
D3	41	51	46	10	0.10
D4	37	43	40	6	0.17
D5	67	76	71.5	9	0.11
D6	26	27	26.5	1	1.00
(a) D9	55	65	60	10	0.10
D10	40	44	42	4	0.25
(a) D12	45	48	46.5	3	0.33
D13	47	51	49	4	0.25
D15	82	84	83	2	0.50
(a) D16	68	76	72	8	0.13
D17	76	81	78.5	5	0.20
D18	72	79	75.5	7	0.14
D19	60	66	63	6	0.17
D22	56	63	59.5	7	0.14
(d) D26	69	75	72	6	0.17
(c) D27	76	81	78.5	5	0.20
(b) D28	86	93	89.5	7	0.14
D29	78	83	80.5	5	0.20
D30	81	84	82.5	3	0.33
D31	72	77	75.5	5	0.20
D32	84	89	86.5	5	0.20
D33	77	84	80.5	7	0.14
D34	84	89	86.5	5	0.20
D35	86	95	90.5	9	0.11

Table XXII con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δt
D36	82	89	85.5	7	0.14
D37	77	80	78.5	3	0.33
D38	81	88	84.5	7	0.14
D39	84	90	87	6	0.17
D40	81	86	83.5	5	0.20
D41	79	85	82	6	0.17
D42	80	85	82.5	5	0.20
D43	70	76	73	6	0.17
D44	88	93	90.5	5	0.20
D45	87	91	89	4	0.25
D46	65	70	67.5	5	0.20
D47	62	67	64.5	5	0.20
D48	85	90	87.5	5	0.20
D49	85	90	87.5	5	0.20
D50	83	86	84.5	3	0.33
D51	75	80	77.5	5	0.20
D52	72	76	74	4	0.25
D53	82	84	83	2	0.50
D54	85	88	86.5	3	0.33
D55	85	90	87.5	5	0.20
D56	76	82	79	6	0.17
D57	80	87	83.5	7	0.14
D58	74	80	77	6	0.17
D59	65	73	69	8	0.13
D60	88	92	90	4	0.25

Table XXII con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δ t C°	1/Δ t
D61	73	80	76.5	7	0.14
D62	78	84	81	6	0.17
D63	78	82	80	4	0.25
D64	80	85	82.5	5	0.20
G1	70	77	73.5	7	0.14
G2	61	67	64	6	0.17
G3	75	80	77.5	5	0.20
G4	63	70	66.5	7	0.14
G5	77	81	79	4	0.25
G6	87	90	88.5	3	0.33
G7	86	91	88.5	5	0.20
G8	80	84	82	4	0.25
G9	79	85	82	6	0.17
G10	48	55	51.5	7	0.14
G11	80	85	82.5	5	0.20
G12	80	87	83.5	7	0.14
G13	74	80	77	6	0.17
G14	75	81	78	6	0.17
G15	19	20	19.5	1	1.00
G16	58	72	65	14	0.07
G17	23	26	24.5	3	0.33
G18	90	90	90	0	

Table XXIII

Copper - conditions for first appearance of needles

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	△ t C°	1/△ t
D3	41	51	46	10	0.10
D4	37	43	40	6	0.17
D5	50	52	51	2	0.50
D6	27	28	27.5	1	1.00
(a) D9	29	31	30	2	0.50
D10	44	47	45.5	3	0.33
(a) D12	34	36	35	2	0.50
D13	47	51	49	4	0.25
D15	82	84	83	2	0.50
(a) D16	63	68	65.5	5	0.20
D17	72	76	74	4	0.25
D18	72	79	75.5	7	0.14
D19	55	59	57	4	0.25
D22	45	51	48	6	0.17
(d) D26	69	75	72	6	0.17
(c) D27	67	71	69	4	0.25
(b) D28	71	78	74.5	7	0.14
D29	71	75	73	4	0.25
D30	54	58	56	4	0.25
D31	62	68	65	6	0.17
D32	78	84	81	6	0.17
D33	77	84	80.5	7	0.14
D34	72	77	74.5	5	0.20
D35	68	72	70	4	0.25

Table XXIII con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δ t C°	1/Δt
D36	75	82	78.5	7	0.14
D37	60	65	62.5	5	0.20
D38	81	88	84.5	7	0.14
D39	79	84	81.5	5	0.20
D40	67	72	69.5	5	0.20
D41	63	68	65.5	5	0.20
D42	59	65	62	6	0.17
D43	70	76	73	6	0.17
D44	63	67	65	4	0.25
D45	67	71	69	4	0.25
D46	58	65	61.5	7	0.14
D47	38	40	39	2	0.50
D48	71	75	73	4	0.25
D49	68	75	71.5	7	0.14
D50	81	83	82	2	0.50
D51	75	80	77.5	5	0.20
D52	72	76	74	4	0.25
D53	64	68	66	4	0.25
D54	72	77	74.5	5	0.20
D55	80	85	82.5	5	0.20
D56	76	82	79	6	0.17
D57	68	72	70	4	0.25
D58	60	65	62.5	5	0.20
D59	55	60	57.5	5	0.20
D60	72	76	74	4	0.25

Table XXIII con't

Run No.	Outlet Temp ^oC	Inlet Temp ^oC	Ave. Temp ^oC	Δt C^o	$1/\Delta t$
D61	65	70	67.5	5	0.20
D62	73	78	75.5	5	0.20
D63	73	80	76.5	7	0.14
D64	80	85	82.5	5	0.20
G1	70	77	73.5	7	0.14
G2	61	67	64	6	0.17
G3	75	80	77.5	5	0.20
G4	63	70	66.5	7	0.14
G5	66	72	69	6	0.17
G6	78	82	80	4	0.25
G7	67	74	70.5	7	0.14
G8	80	84	82	4	0.25
G9	67	74	70.5	7	0.14
G10	48	55	51.5	7	0.14
G11	49	56	52.5	7	0.14
G12	51	58	54.5	7	0.14
G13	30	36	33	6	0.17
G14	67	71	69	4	0.25
G15	20	21	20.5	1	1.00
G16	27	31	29	4	0.25
G17	23	26	24.5	3	0.33
G18	32	35	33.5	3	0.33

Table XXIV

Copper - conditions for first appearance of octagons

Run No.	Outlet Temp ^{o}C	Inlet Temp ^{o}C	Ave. Temp ^{o}C	Δt C^{o}	$1/\Delta t$
(a) D9	51	55	53	4	0.25
D10	30	31	30.5	1	1.00
D12	38	41	39.5	3	0.33
(a) D16	59	63	61	4	0.25
D17	47	51	49	4	0.25
D18	61	67	64	6	0.17
D19	59	65	62	6	0.17
(c) D27	52	56	54	4	0.25
D29	40	42	41	2	0.50
D30	58	62	60	4	0.25
D31	50	53	51.5	3	0.33
D32	52	56	54	4	0.25
D35	61	66	63.5	5	0.20
D37	55	60	57.5	5	0.20
D38	49	52	50.5	3	0.33
D40	37	39	38	2	0.50
D41	47	51	49	4	0.25
D42	46	50	48	4	0.25
D44	46	49	45.5	3	0.33
D47	58	62	60	4	0.25
D49	38	40	39	2	0.50
D52	56	60	58	4	0.25
D55	45	48	46.5	3	0.33
D57	50	54	52	4	0.25

Table XXIV con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	△ t C°	1/△ t
D58	60	65	62.5	5	0.20
D60	54	58	56	4	0.25
D63	50	54	52	4	0.25
G2	61	67	64	6	0.17
G4	58	63	60.5	5	0.20
G5	54	59	56.5	5	0.20
G6	52	56	54	4	0.25
G7	40	43	41.5	3	0.33
G8	44	48	46	4	0.25
G11	45	49	47	4	0.25
G16	58	72	65	14	0.07
G18	90	90	90	0	

Table XXV

Copper - conditions for first appearance of pentagons

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δ t C°	1/Δ t
D4	24	26	25	2	0.50
(a) D9	38	45	41.5	7	0.14
D10	34	37	35.5	3	0.33
(a) D12	36	38	37	2	0.50
D13	47	51	49	4	0.25
(a) D16	59	63	61	4	0.25
D17	72	76	74	4	0.25
D18	61	67	64	6	0.17
D19	36	38	37	2	0.50
D29	71	75	73	4	0.25
D30	65	69	67	4	0.25
D31	50	53	51.5	3	0.33
D32	52	56	54	4	0.25
D33	59	65	62	6	0.17
D34	50	56	53	6	0.17
D36	54	60	58	4	0.25
D37	55	60	57.5	5	0.20
D38	55	60	57.5	5	0.20
D39	65	69	67	4	0.25
D41	51	57	54	6	0.17
D43	43	48	45.5	5	0.20
D45	52	56	54	4	0.25
D46	43	47	45	4	0.25
D47	44	46	45	2	0.50

Table XXV con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δ t C°	1/Δ t
D51	50	56	53	6	0.17
D54	56	60	58	4	0.25
D56	37	44	40.5	7	0.14
D57	63	68	65.5	5	0.20
D58	47	51	49	4	0.25
D61	56	62	59	6	0.17
D62	54	59	56.5	5	0.20
D64	55	59	57	4	0.25
G1	38	42	40	4	0.25
G2	39	44	41.5	5	0.20
G3	56	62	59	6	0.17
G4	44	49	46.5	5	0.20
G5	59	63	61	4	0.25
G6	56	61	58.5	5	0.20
G7	43	48	45.5	5	0.20
G8	44	48	46	4	0.25
G11	45	49	47	4	0.25
G14	45	50	47.5	5	0.20
G15	17	17	17	0	
G16	40	48	44	8	0.13
G18	70	86	78	16	0.06

Table XXVI

Copper - Conditions for first appearance of rods

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δ t C°	1/Δ t
D3	41	51	46	10	0.10
D4	37	43	40	6	0.17
D5	67	76	71.5	9	0.11
D6	26	27	26.5	1	1.00
(a) D9	65	71	68	6	0.17
D10	44	47	45.5	3	0.33
(a) D12	45	48	46.5	3	0.33
D13	47	51	49	4	0.25
D15	82	84	83	2	0.50
(a) D16	68	76	72	8	0.13
D17	76	81	78.5	5	0.20
D18	72	77	75.5	7	0.14
D19	81	91	86	10	0.10
D22	51	57	54	6	0.17
(d) D26	69	75	72	6	0.17
(c) D27	76	81	78.5	5	0.20
(b) D28	78	86	82	8	0.13
D29	71	75	73	4	0.25
D30	75	78	76.5	3	0.33
D31	73	78	75.5	5	0.20
D32	72	78	75	6	0.17
D33	77	84	80.5	7	0.14
D34	77	84	80.5	7	0.14
D35	68	72	70	4	0.25

Table XXVI con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δ t
D36	68	75	71.5	7	0.14
D37	60	65	62.5	5	0.20
D38	81	88	84.5	7	0.14
D39	79	84	81.5	5	0.20
D40	67	72	69.5	5	0.20
D41	68	75	71.5	7	0.14
D42	59	65	62	6	0.17
D43	70	76	73	6	0.17
D44	72	76	74	4	0.25
D45	71	75	73	4	0.25
D46	58	65	61.5	7	0.14
D47	62	67	64.5	5	0.20
D48	71	75	73	4	0.25
D49	80	85	82.5	5	0.20
D50	81	83	82	2	0.50
D51	70	75	72.5	5	0.20
D52	72	76	74	4	0.25
D53	78	82	80	4	0.25
D54	72	77	74.5	5	0.20
D55	76	80	78	4	0.25
D56	76	82	79	6	0.17
D57	68	72	70	4	0.25
D58	60	65	62.5	5	0.20
D59	60	65	62.5	5	0.20
D60	74	82	78	8	0.13

Table XXVI con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
D61	70	73	71.5	3	0.33
D62	78	84	81	6	0.17
D63	71	78	74.5	7	0.14
D64	75	80	77.5	5	0.20
G1	70	77	73.5	7	0.14
G2	61	67	64	6	0.17
G3	75	80	77.5	5	0.20
G4	63	70	66.5	7	0.14
G5	72	77	74.5	5	0.20
G6	78	82	80	4	0.25
G7	74	81	77.5	7	0.14
G8	80	84	82	4	0.25
G9	67	74	70.5	7	0.14
G10	48	55	51.5	7	0.14
G11	56	64	60	8	0.13
G12	51	58	54.5	7	0.14
G13	36	44	40	8	0.13
G14	67	71	69	4	0.25
G15	20	21	20.5	1	1.00
G16	58	72	65	14	0.07
G17	23	26	24.5	3	0.33
G18	48	57	52.5	9	0.11

Table XXVII

Copper - conditions for first appearance of squares

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	△t C°	1/△t
D3	5	5	5	0	
D4	37	43	40	6	0.17
D5	33	34	33.5	1	1.00
D6	26	27	26.5	1	1.00
(a) D9	51	55	53	4	0.25
D10	40	44	42	4	0.25
(a) D12	45	48	46.5	3	0.33
D13	41	44	42.5	3	0.33
D15	82	84	83	2	0.50
(a) D16	68	76	72	8	0.13
D17	76	81	78.5	5	0.20
D18	61	67	64	6	0.17
D19	60	65	62.5	5	0.20
D22	45	51	48	6	0.17
(d) D26	65	69	67	4	0.25
(c) D27	30	31	30.5	1	1.00
(b) D28	78	86	82	8	0.13
D29	71	75	73	4	0.25
D30	78	81	79.5	3	0.33
D31	62	68	65	6	0.17
D32	56	61	58.5	5	0.20
D33	65	70	67.5	5	0.20
D34	66	72	69	6	0.17
D35	48	53	50.5	5	0.20

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
D36	62	68	65	6	0.17
D37	74	77	75.5	3	0.33
D38	69	75	72	6	0.17
D39	75	79	77	4	0.25
D40	67	73	70	6	0.17
D41	75	79	77	4	0.25
D42	46	50	48	4	0.25
D43	60	65	62.5	5	0.20
D44	67	72	69.5	5	0.20
D45	67	71	69	4	0.25
D46	58	65	61.5	7	0.14
D47	58	62	60	4	0.25
D48	52	56	54	4	0.25
D49	58	64	61	6	0.17
D50	81	83	82	2	0.50
D51	56	60	58	4	0.25
D52	72	76	74	4	0.25
D53	82	84	83	2	0.50
D54	81	85	83	4	0.25
D55	76	80	78	4	0.25
D56	52	60	56	8	0.13
D57	68	72	70	4	0.25
D58	56	60	58	4	0.25
D59	51	55	53	4	0.25
D60	63	69	66	6	0.17
D61	56	62	59	6	0.17

Table XXVII con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	△t C°	1/△t
D62	54	59	56.5	5	0.20
D63	50	54	52	4	0.25
D64	71	75	73	4	0.25
G1	48	54	51	6	0.17
G2	39	44	41.5	5	0.20
G3	56	62	59	6	0.17
G4	45	50	47.5	5	0.20
G5	66	72	69	6	0.17
G6	64	69	66.5	5	0.20
G7	55	62	58.5	7	0.14
G8	44	48	46	4	0.25
G9	53	60	56.5	7	0.14
G11	45	49	47	4	0.25
G14	45	50	47.5	5	0.20
G15	20	21	20.5	1	1.00
G16	49	58	53.5	9	0.11
G17	23	26	24.5	3	0.33
G18	86	90	88	4	0.25

Table XXVIII

Copper - conditions for first appearance of trapezoids

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δ t C°	1/Δ t
D3	41	51	46	10	0.10
D4	37	43	40	6	0.17
D5	33	34	33.5	1	1.00
D10	42	42	42	0	
(a) D12	38	41	39.5	3	0.30
D13	47	51	49	4	0.25
D15	82	84	83	2	0.50
(a) D16	68	76	72	8	0.13
D17	72	76	74	4	0.25
D18	61	67	64	6	0.17
D19	65	72	68.5	7	0.14
D22	63	70	66.5	7	0.14
(d) D26	55	60	57.5	5	0.20
(c) D27	63	67	65	4	0.25
(b) D28	71	78	74.5	7	0.14
D29	71	75	73	4	0.25
D30	58	62	60	4	0.25
D31	48	50	49	2	0.50
D32	56	61	58.5	5	0.20
D33	44	49	46.5	5	0.20
D34	50	50	53	6	0.17
D35	68	72	70	4	0.25
D36	68	75	71.5	7	0.14
D37	48	51	49.5	3	0.33

Table XXVIII con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
D38	52	55	53.5	3	0.33
D39	50	52	51	2	0.50
D40	52	56	54	4	0.25
D41	51	57	54	6	0.17
D42	59	65	62	6	0.17
D43	60	65	62.5	5	0.20
D44	63	67	65	4	0.25
D45	61	67	64	6	0.17
D46	58	65	61.5	7	0.14
D48	52	56	54	4	0.25
D49	68	75	71.5	7	0.14
D50	50	55	52.5	5	0.20
D51	56	60	58	4	0.25
D52	49	53	51	4	0.25
D53	45	47	46	2	0.50
D55	50	53	51.5	3	0.33
D56	44	52	48	8	0.13
D57	54	57	55.5	3	0.33
D58	56	60	58	4	0.25
D59	51	55	53	4	0.25
D61	56	62	59	6	0.17
D62	62	68	65	6	0.17
D63	58	63	60.5	5	0.20
D64	67	71	69	4	0.25
G1	63	70	66.5	7	0.14

Table XXVIII con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
G2	61	67	64	6	0.17
G3	56	62	59	6	0.17
G4	63	70	66.5	7	0.14
G5	66	72	69	6	0.17
G6	64	69	66.5	5	0.20
G7	63	68	64.5	5	0.20
G8	55	61	58	6	0.17
G9	60	67	63.5	7	0.14
G11	56	64	60	8	0.13
G12	58	64	61	6	0.17
G13	52	60	56	8	0.13
G14	57	61	59	4	0.25
G16	18	18	18	0	
G17	21	23	22	2	0.50
G18	57	70	63.5	13	0.08

Table XXIX

Copper - conditions for first appearance of triangles

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	△ t C°	1/△ t
D3	41	51	46	10	0.10
D4	37	43	40	6	0.17
D5	67	76	71.5	9	0.11
D6	26	27	26.5	1	1.00
(a) D9	51	55	53	4	0.25
D10	44	47	45.5	3	0.33
(a) D12	45	48	46.5	3	0.33
D13	47	51	49	4	0.25
D15	82	84	83	2	0.50
(a) D16	68	76	72	8	0.13
D17	72	76	74	4	0.25
D18	72	79	75.5	7	0.14
D19	81	91	86	10	0.10
D22	63	70	66.5	7	0.14
(d) D26	65	69	67	4	0.25
(c) D27	67	73	70	6	0.17
(b) D28	78	86	82	8	0.13
D29	75	78	76.5	3	0.33
D30	81	84	82.5	3	0.33
D31	73	78	75.5	5	0.20
D32	78	84	81	6	0.17
D33	77	84	80.5	7	0.14
D34	84	89	86.5	5	0.20
D35	79	86	82.5	7	0.14

Table XXIX con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δ t C°	1/Δ t
D36	75	82	78.5	7	0.14
D37	77	80	78.5	3	0.33
D38	75	81	78	6	0.17
D39	84	90	87	6	0.17
D40	81	86	83.5	5	0.20
D41	79	85	82	6	0.17
D42	80	85	82.5	5	0.20
D43	70	76	73	6	0.17
D44	81	88	84.5	7	0.14
D45	78	82	80	4	0.25
D46	65	70	67.5	5	0.20
D47	62	67	64.5	5	0.20
D48	85	90	87.5	5	0.20
D49	85	90	87.5	5	0.20
D50	81	83	82	2	0.50
D51	80	85	82.5	5	0.20
D52	72	76	74	4	0.25
D53	82	84	83	2	0.50
D54	81	85	83	4	0.25
D55	80	85	82.5	5	0.20
D56	76	82	79	6	0.17
D57	80	87	83.5	7	0.14
D58	74	80	77	6	0.17
D59	73	80	76.5	7	0.14
D60	88	92	90	4	0.25

Table XXIX con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δ t C°	1/Δ t
D61	73	80	76.5	7	0.14
D62	78	84	81	6	0.17
D63	78	82	80	4	0.25
D64	80	85	82.5	5	0.20
G1	70	77	73.5	7	0.14
G2	61	67	64	6	0.17
G3	75	80	77.5	5	0.20
G4	63	70	66.5	7	0.14
G5	72	77	74.5	5	0.20
G6	87	90	88.5	3	0.33
G7	86	91	88.5	5	0.20
G8	80	84	82	4	0.25
G9	79	85	82	6	0.17
G10	48	55	51.5	7	0.14
G11	80	85	82.5	5	0.20
G12	72	80	76	8	0.13
G13	74	80	77	6	0.17
G14	68	75	71.5	7	0.14
G16	58	72	65	14	0.07
G17	23	26	24.5	3	0.33
G18	86	90	88	4	0.25

Table XXX

Copper - conditions for first appearance of truncated diamonds

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
D3	29	41	35	12	0.08
D4	31	37	34	6	0.17
D10	29	30	29.5	1	1.00
D13	44	47	45.5	3	0.33
D15	61	66	63.5	5	0.20
D17	67	72	69.5	5	0.20
D18	61	67	64	6	0.17
D19	60	66	63	6	0.17
D22	40	44	42	4	0.25
(d) D26	65	69	67	4	0.25
(c) D27	63	67	65	4	0.25
(b) D28	53	59	56	6	0.17
D31	61	67	64	6	0.17
D33	44	49	46.5	5	0.20
D37	44	48	46	4	0.25
D43	55	60	57.5	5	0.20
D46	58	65	61.5	7	0.14
D48	38	40	39	2	0.50
D49	58	64	61	6	0.17
D50	46	50	48	4	0.25
D52	39	41	40	2	0.50
D53	38	40	39	2	0.50
D56	60	70	65	10	0.10
D57	50	54	52	4	0.25

Table XXX con't

Run No..	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δt
D58	51	56	53.5	5	0.20
D59	37	40	38.5	3	0.33
D63	29	31	30	2	0.50
G2	39	44	41.5	5	0.20
G3	50	56	53	6	0.17
G4	58	63	60.5	5	0.20
G5	54	59	56.5	5	0.20
G6	56	61	58.5	5	0.20
G7	43	48	45.5	5	0.20
G11	45	49	47	4	0.25
G14	31	35	33	4	0.25
G15	19	20	19.5	1	1.00
G16	49	58	53.5	9	0.11
G17	23	26	24.5	3	0.33
G18	76	80	78	4	0.25

Table XXXI

Silver - conditions for the first appearance of bent wires

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta$t
E19	48	54	51	6	0.17
E23	43	46	44.5	3	0.33
E35	45	49	47	4	0.25
E36	56	59	57.5	3	0.33
E37	47	52	49.5	5	0.20
E39	46	49	47.5	3	0.33
E42	47	50	48.5	3	0.33
E45	50	56	53	6	0.17
E46	49	53	51	4	0.25
E51	51	56	53.5	5	0.20
H5	50	55	52.5	5	0.20
H6	49	54	51.5	5	0.20
H7	53	57	55	4	0.25
H8	49	54	51.5	5	0.20
H9	44	48	46	4	0.25
H10	47	50	48.5	3	0.33
J3	47	52	49.5	5	0.20
J4	50	54	52	4	0.25
J5	50	54	52	4	0.25
J6	48	52	50	4	0.25
J7	50	56	53	6	0.17
J8	48	52	50	4	0.25
J9	47	53	49.5	5	0.20
J15	50	54	52	4	0.25

Table XXXII

Silver - conditions for the first appearance of dendrites

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	△t C°	1/△t
E13	29	30	29.5	1	1.00
E20	39	41	40	2	0.50
E33	23	24	23.5	1	1.00
E35	29	31	30	2	0.50
E39	39	41	40	2	0.50
E43	28	29	28.5	1	1.00
E47	24	25	24.5	1	1.00

Table XXXIII

Silver - conditions for the first appearance of diamonds

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
E13	95	95	95	0	
E20	48	52	50	4	0.25
E22	62	69	65.5	7	0.14
E34	64	70	67	6	0.17
E36	64	68	66	4	0.25
E37	57	63	60	6	0.17
E39	60	64	62	4	0.25
E42	58	63	60.5	5	0.20
E45	61	67	64	6	0.17
E46	70	74	72	4	0.25
E47	68	73	70.5	5	0.20
E49	55	60	57.5	5	0.20
E51	51	56	53.5	5	0.20
H3	58	64	61	6	0.17
H5	70	75	72.5	5	0.20
H6	66	71	68.5	5	0.20
H7	66	71	68.5	5	0.20
H8	54	60	57	6	0.17
H10	55	60	57.5	5	0.20
J1	60	66	63	6	0.17
J2	55	62	58.5	7	0.14
J3	58	64	61	6	0.17
J4	65	71	68	6	0.17
J5	71	75	73	4	0.25

Table XXXIII con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
J6	62	67	64.5	5	0.20
J7	65	69	67	4	0.25
J8	71	75	73	4	0.25
J9	55	60	57.5	5	0.20
J10	65	71	68	6	0.17
J12	60	65	62.5	5	0.20
J13	65	71	68	6	0.17

Table XXXIV

Silver - conditions for the first appearance of hexagons

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δ t C°	1/Δ t
E12	77	83	80	6	0.17
E13	95	95	95	0	
E14	78	84	81	6	0.17
E15	67	73	70	6	0.17
E16	55	60	57.5	5	0.20
E17	48	55	51.5	7	0.14
E18	60	65	62.5	5	0.20
E19	76	83	79.5	7	0.14
E20	70	76	73	6	0.17
E21	60	66	63	6	0.17
E22	68	77	72.5	9	0.11
E23	43	46	44.5	3	0.33
E24	56	64	60	8	0.13
E25	51	58	54.5	7	0.14
E26	70	76	73	6	0.17
E27	47	50	48.5	3	0.33
E28	56	64	60	8	0.13
E29	76	85	80.5	9	0.11
E30	67	75	71	8	0.13
E31	69	75	72	6	0.17
E32	78	84	81	6	0.17
E33	68	74	71	6	0.17
E34	70	78	74	8	0.13
E35	58	65	61.5	7	0.14

Table XXXIV con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	△ t C°	1/△ t
E36	68	72	70	4	0.25
E37	68	73	70.5	5	0.20
E38	69	75	72	6	0.17
E39	60	64	62	4	0.25
E40	77	86	81.5	9	0.11
E41	57	65	61	8	0.13
E42	78	83	80.5	5	0.20
E43	65	74	69.5	9	0.11
E44	74	80	77	6	0.17
E45	71	76	73.5	5	0.20
E46	79	86	82.5	7	0.14
E47	72	77	74.5	5	0.20
E48	55	63	59	8	0.13
E49	65	71	68	6	0.17
E50	77	83	80	6	0.17
E51	72	79	75.5	7	0.14
E52	68	76	72	8	0.13
H1	71	80	75.5	9	0.11
H2	62	69	65.5	7	0.14
H3	77	85	81	8	0.13
H4	74	80	77	6	0.17
H5	80	86	83	6	0.17
H6	80	85	82.5	5	0.20
H7	81	87	84	6	0.17
H8	76	82	79	6	0.17

Table XXXIV con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
H9	70	75	72.5	5	0.20
H10	72	77	74.5	5	0.20
J1	77	83	80	6	0.17
J2	74	80	77	6	0.17
J3	79	85	82	6	0.17
J4	76	81	78.5	5	0.20
J5	79	84	81.5	5	0.20
J6	70	75	72.5	5	0.20
J7	76	81	78.5	5	0.20
J8	78	83	80.5	5	0.20
J9	80	85	82.5	5	0.20
J10	76	84	80	8	0.13
J11	75	81	78	6	0.17
J12	78	84	81	6	0.17
J13	78	84	81	6	0.17
J14	82	87	84.5	5	0.20
J15	69	73	71	4	0.25

Table XXXV

Silver - conditions for the first appearance of needles

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
E19	42	45	43.5	3	0.33
E20	25	26	25.5	1	1.00
E32	24	27	25.5	3	0.33
E33	29	31	30	2	0.50
E35	29	31	30	2	0.50
E39	39	41	40	2	0.50
E42	36	39	37.5	3	0.33
E43	37	40	38.5	3	0.33
E47	22	23	22.5	1	1.00
J7	40	43	41.5	3	0.33

Table XXXVI

Silver - conditions for the first appearance of octagons

Run No.	Outlet Temp ^{o}C	Inlet Temp ^{o}C	Ave. Temp ^{o}C	Δ t C^{o}	1/Δ t
E13	92	95	93.5	3	0.33
E14	56	61	58.5	5	0.20
E15	62	67	64.5	5	0.20
E19	76	83	79.5	7	0.14
E20	65	70	67.5	5	0.20
E21	48	54	51	6	0.17
E23	38	40	39	2	0.50
E26	70	76	73	6	0.17
E29	85	91	88	6	0.17
E32	63	68	65.5	5	0.20
E33	68	74	71	6	0.17
E34	59	64	61.5	5	0.20
E35	45	49	47	4	0.25
E36	64	68	66	4	0.25
E39	46	49	47.5	3	0.33
E41	48	51	49.5	3	0.33
E44	52	56	54	4	0.25
E45	50	56	53	6	0.17
E46	70	74	72	4	0.25
E47	63	67	65	4	0.25
E49	55	60	57.5	5	0.20
H1	65	71	68	6	0.17
H3	58	64	61	6	0.17
H5	70	75	72.5	5	0.20

Table XXXVI con't

Run No.	Outlet Temp ^{o}C	Inlet Temp ^{o}C	Ave. Temp ^{o}C	Δt C^{o}	$1/\Delta t$
H6	66	71	68.5	5	0.20
H7	71	77	74	6	0.17
H8	45	49	47	4	0.25
H9	53	58	55.5	5	0.20
H10	47	50	48.5	3	0.33
J1	66	70	68	4	0.25
J2	62	67	64.5	5	0.20
J3	79	85	82	6	0.17
J4	72	77	73.5	5	0.20
J5	75	79	77	4	0.25
J6	75	79	77	4	0.25
J7	50	56	53	6	0.17
J8	63	67	65	4	0.25
J9	55	60	57.5	5	0.20
J10	65	71	68	6	0.17
J12	49	55	52	6	0.17
J13	52	58	55	6	0.17
J14	61	65	63	4	0.25
J15	65	69	67	4	0.25

Table XXXVII

Silver - conditions for the first appearance of pentagons

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δt
E14	41	44	42.5	3	0.33
E21	38	41	39.5	3	0.33
E22	68	77	72.5	9	0.11
E23	38	40	39	2	0.50
E24	40	44	42	4	0.25
E25	46	51	48.5	5	0.20
E28	51	56	53.5	5	0.20
E29	68	76	72	8	0.13
E30	54	61	57.5	7	0.14
E31	57	63	60.5	7	0.14
E32	68	77	72.5	9	0.11
E33	59	66	62.5	7	0.14
E35	45	49	47	4	0.25
E37	57	63	60	6	0.17
E38	61	69	65	8	0.13
E42	43	47	45	4	0.25
E44	56	63	59.5	7	0.14
E47	52	58	55	6	0.17
E51	64	72	68	8	0.13
H2	62	69	65.5	7	0.14
H4	60	67	63.5	7	0.14
H5	50	55	52.5	5	0.20
H6	49	54	51.5	5	0.20
H7	57	63	60	6	0.17

Table XXXVII con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δ t C°	1/Δ t
H8	49	54	51.5	5	0.20
H9	44	48	46	4	0.25
H10	50	55	52.5	5	0.20
J3	47	52	49.5	5	0.20
J7	40	43	41.5	3	0.33
J10	49	54	51.5	5	0.20
J11	61	68	64.5	7	0.14
J13	52	58	55	6	0.17
J15	46	50	48	4	0.25

Table XXXVIII

Silver - conditions for the first appearance of rods

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δ t
E12	77	83	80	6	0.17
E13	95	95	95	0	
E14	64	72	68	8	0.13
E15	58	62	60	4	0.25
E16	51	55	53	4	0.25
E17	48	55	51.5	7	0.14
E18	60	65	62.5	5	0.20
E19	76	83	79.5	7	0.14
E20	70	76	73	6	0.17
E21	54	60	57	6	0.17
E22	61	68	64.5	7	0.14
E23	43	46	44.5	3	0.33
E24	56	64	60	8	0.13
E25	46	51	48.5	5	0.20
E26	70	76	73	6	0.17
E27	47	50	48.5	3	0.33
E28	56	64	60	8	0.13
E29	76	85	80.5	9	0.11
E30	67	75	71	8	0.13
E31	57	63	60.5	7	0.14
E32	63	68	65.5	5	0.20
E33	68	74	71	6	0.17
E34	70	78	74	8	0.13
E35	58	65	61.5	7	0.14

Table XXXVIII con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	△ t C°	1/△ t
E36	68	72	70	4	0.25
E37	68	73	70.5	5	0.20
E38	69	75	72	6	0.17
E39	60	64	62	4	0.25
E40	69	77	73	8	0.13
E41	57	65	61	8	0.13
E42	78	83	80.5	5	0.20
E43	57	65	61	8	0.13
E44	74	80	77	6	0.17
E45	71	76	73.5	5	0.20
E46	79	86	82.5	7	0.14
E47	67	71	69	4	0.25
E48	55	63	59	8	0.13
E49	65	71	68	6	0.17
E50	77	83	80	6	0.17
E51	72	79	75.5	7	0.14
E52	68	76	72	8	0.13
H1	65	71	68	6	0.17
H2	62	69	65.5	7	0.14
H3	64	70	67	6	0.17
H4	74	80	77	6	0.17
H5	75	80	77.5	5	0.20
H6	71	76	73.5	5	0.20
H7	71	77	74	6	0.17
H8	76	82	79	6	0.17

Table XXXVIII con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	△t C°	1/△t
H9	66	70	68	4	0.25
H10	72	77	74.5	5	0.20
J1	77	83	80	6	0.17
J2	74	80	77	6	0.17
J3	74	79	76.5	5	0.20
J4	71	76	73.5	5	0.20
J5	63	67	65	4	0.25
J6	70	75	72.5	5	0.20
J7	76	81	78.5	5	0.20
J8	78	83	80.5	5	0.20
J9	80	85	82.5	5	0.20
J10	76	84	80	8	0.13
J11	75	81	78	6	0.17
J12	71	78	74.5	7	0.14
J13	71	78	74.5	7	0.14
J14	82	87	84.5	5	0.20
J15	69	73	71	4	0.25

Table XXXIX

Silver - conditions for first appearance of squares

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δ t
E12	65	72	68.5	7	0.14
E13	92	95	93.5	3	0.33
E14	56	61	58.5	5	0.20
E15	58	62	60	4	0.25
E16	55	60	57.5	5	0.20
E17	48	55	51.5	7	0.14
E18	60	65	62.5	5	0.20
E19	62	70	66	8	0.13
E20	70	76	73	6	0.17
E21	44	48	46	4	0.25
E22	54	61	57.5	7	0.14
E23	43	46	44.5	3	0.33
E24	49	56	52.5	7	0.14
E25	46	51	48.5	5	0.20
E26	70	76	73	6	0.17
E27	47	50	48.5	3	0.33
E28	51	56	53.5	5	0.20
E29	64	71	67.5	7	0.14
E30	60	67	63.5	7	0.14
E31	45	51	48	6	0.17
E32	63	68	65.5	5	0.20
E33	52	59	55.5	7	0.14
E34	64	70	67	6	0.17
E35	45	49	47	4	0.25

Table XXXIX con't

Run No.	Outlet Temp ^{o}C	Inlet Temp ^{o}C	Ave. Temp ^{o}C	Δt C^{o}	$1/\Delta t$
E36	52	56	54	4	0.25
E37	57	63	60	6	0.17
E38	54	61	57.5	7	0.14
E39	53	59	55	4	0.25
E41	57	65	61	8	0.13
E42	63	68	65.5	5	0.20
E43	57	65	61	8	0.13
E44	63	69	66	6	0.17
E45	61	67	64	6	0.17
E46	49	53	51	4	0.25
E47	52	58	55	6	0.17
E49	60	65	62.5	5	0.20
E50	62	70	66	8	0.13
E51	51	56	53.5	5	0.20
E52	60	68	64	8	0.13
H1	65	71	68	6	0.17
H2	62	69	65.5	7	0.14
H3	64	70	67	6	0.17
H4	67	74	70.5	7	0.14
H5	65	70	67.5	5	0.20
H6	66	71	68.5	5	0.20
H7	71	77	74	6	0.17
H8	65	71	68	6	0.17
H9	66	70	68	4	0.25
H10	64	69	66.5	5	0.20

Table XXXIX con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
J1	60	66	63	6	0.17
J2	67	74	70.5	7	0.14
J3	74	79	76.5	5	0.20
J4	65	71	68	6	0.17
J5	71	75	73	4	0.25
J6	70	75	72.5	5	0.20
J7	65	69	67	4	0.25
J8	71	75	73	4	0.25
J9	65	70	67.5	5	0.20
J10	65	71	68	6	0.17
J11	61	68	64.5	7	0.14
J12	65	71	68	6	0.17
J13	65	71	68	6	0.17
J14	65	72	68.5	7	0.14
J15	69	73	71	4	0.25

Table XL

Silver - conditions for first appearance of trapezoids

Run No.	Outlet Temp ^oC	Inlet Temp ^oC	Ave. Temp ^oC	Δt C^o	$1/\Delta t$
E12	76	83	79.5	7	0.14
E13	87	93	90	6	0.17
E14	47	50	48.5	3	0.33
E15	55	58	56.5	3	0.33
E16	48	51	49.5	3	0.33
E17	43	48	45.5	5	0.20
E18	41	45	43	4	0.25
E19	42	45	43.5	3	0.33
E20	65	70	67.5	5	0.20
E21	35	38	36.5	3	0.33
E22	61	68	64.5	7	0.14
E23	40	43	41.5	3	0.33
E24	56	64	60	8	0.13
E25	46	51	48.5	5	0.20
E26	60	70	65	10	0.10
E27	47	50	48.5	3	0.33
E28	56	64	60	8	0.13
E29	76	85	80.5	9	0.11
E30	54	61	57.5	7	0.14
E31	57	64	60.5	7	0.14
E32	63	68	65.5	5	0.20
E33	59	68	63.5	9	0.11
E34	70	78	74	8	0.13
E35	52	58	55	6	0.17

Table XL con't

Run No.	Outlet Temp $^{\circ}C$	Inlet Temp $^{\circ}C$	Ave. Temp $^{\circ}C$	Δt C°	$1/\Delta t$
E36	48	52	50	4	0.25
E37	57	63	60	6	0.17
E38	61	69	65	8	0.13
E39	46	49	47.5	3	0.33
E40	69	77	73	8	0.13
E41	57	65	61	8	0.13
E42	63	68	65.5	5	0.20
E43	50	57	53.5	7	0.14
E44	63	69	66	6	0.17
E45	63	69	66	6	0.17
E46	60	65	62.5	5	0.20
E47	58	63	60.5	5	0.20
E49	60	65	62.5	5	0.20
E50	70	77	73.5	7	0.14
E51	56	64	60	8	0.13
E52	60	68	64	8	0.13
H1	57	65	61	8	0.13
H2	62	69	65.5	7	0.14
H3	64	70	67	6	0.17
H4	60	67	63.5	7	0.14
H5	65	70	67.5	5	0.20
H6	66	71	68.5	5	0.20
H7	57	63	60	6	0.17
H8	76	82	79	6	0.17
H9	58	62	60	4	0.25

Table XL con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δt
H10	64	69	66.5	5	0.20
J1	77	83	80	6	0.17
J2	55	62	58.5	7	0.14
J3	58	64	61	6	0.17
J4	59	65	62	6	0.17
J5	63	67	65	4	0.25
J6	62	67	64.5	5	0.20
J7	65	69	67	4	0.25
J8	67	71	69	4	0.25
J9	65	70	67.5	5	0.20
J10	65	71	68	6	0.17
J11	68	75	71.5	7	0.14
J12	71	78	74.5	7	0.14
J13	58	65	61.5	7	0.14
J14	57	61	59	4	0.25
J15	65	69	67	4	0.25

Table XLI

Silver - conditions for first appearance of triangles

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δ t
E12	76	83	79.5	7	0.14
E13	95	95	95	0	
E14	72	78	75	6	0.17
E15	58	62	60	4	0.25
E16	51	55	53	4	0.25
E17	48	55	51.5	7	0.14
E18	51	56	53.5	5	0.20
E19	76	83	79.5	7	0.14
E20	65	70	67.5	5	0.20
E21	41	44	42.5	3	0.33
E22	48	54	51	6	0.17
E23	40	43	41.5	3	0.33
E24	56	64	60	8	0.13
E25	36	40	38	4	0.25
E26	60	70	65	10	0.10
E27	47	50	48.5	3	0.33
E28	51	56	53.5	5	0.20
E29	58	66	62	8	0.13
E30	60	67	63.5	7	0.14
E31	57	64	60.5	7	0.14
E32	68	77	72.5	9	0.11
E33	68	74	71	6	0.17
E34	70	78	74	8	0.13
E35	58	65	61.5	7	0.14

Table XLI con't

Run No.	Outlet Temp ^{o}C	Inlet Temp ^{o}C	Ave. Temp ^{o}C	Δt C^{o}	$1/\Delta t$
E36	52	56	54	4	0.25
E37	63	68	65.5	5	0.20
E38	61	69	65	8	0.13
E39	53	57	55	4	0.25
E40	69	77	73	8	0.13
E41	50	57	53.5	7	0.14
E42	68	73	70.5	5	0.20
E43	65	74	69.5	9	0.11
E44	63	69	66	6	0.17
E45	61	67	64	6	0.17
E46	53	60	56.5	7	0.14
E47	52	58	55	6	0.17
E48	55	63	59	8	0.13
E49	65	71	68	6	0.17
E50	70	77	73.5	7	0.14
E51	72	79	75.5	7	0.14
E52	68	76	72	8	0.13
H1	65	71	68	6	0.17
H2	62	69	65.5	7	0.14
H3	75	83	79	8	0.13
H4	74	80	77	6	0.17
H5	75	80	77.5	5	0.20
H6	76	80	78	4	0.25
H7	71	77	74	6	0.17
H8	76	82	79	6	0.17

Table XLI con't

Run No.	Outlet Temp ^{o}C	Inlet Temp ^{o}C	Ave. Temp ^{o}C	Δt C^{o}	$1/\Delta t$
H9	75	79	77	4	0.25
H10	73	78	75.5	5	0.20
J1	70	77	73.5	7	0.14
J2	67	74	70.5	7	0.14
J3	74	79	76.5	5	0.20
J4	65	71	68	6	0.17
J5	79	84	81.5	5	0.20
J6	70	75	72.5	5	0.20
J7	76	81	78.5	5	0.20
J8	78	83	80.5	5	0.20
J9	75	80	77.5	5	0.20
J10	71	76	73.5	5	0.20
J11	61	68	64.5	7	0.14
J12	65	71	68	6	0.17
J13	65	71	68	6	0.17
J14	78	82	80	4	0.25
J15	79	82	80.5	3	0.33

Table XLII

Silver - conditions for first appearance of truncated diamonds

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δt
E12	73	77	75	4	0.25
E13	87	93	90	6	0.17
E14	50	52	51	2	0.50
E15	58	62	60	4	0.25
E16	35	38	36.5	3	0.33
E17	48	55	51.5	7	0.14
E18	45	51	48	6	0.17
E19	48	54	51	6	0.17
E20	35	38	36.5	3	0.33
E22	38	43	40.5	5	0.20
E23	43	46	44.5	3	0.33
E24	40	44	42	4	0.25
E25	31	34	32.5	3	0.33
E26	43	52	47.5	9	0.11
E27	47	50	48.5	3	0.33
E28	33	41	37	8	0.13
E29	30	35	32.5	5	0.20
E31	57	64	60.5	7	0.14
E32	57	63	60	6	0.17
E33	52	59	55.5	7	0.14
E34	64	70	67	6	0.17
E35	45	49	47	4	0.25
E36	68	72	70	4	0.25
E37	68	73	70.5	5	0.20

Table XLII con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δ t
E38	61	69	65	8	0.13
E39	49	53	51	4	0.25
E40	34	41	37.5	7	0.14
E41	42	50	46	8	0.13
E42	68	73	70.5	5	0.20
E43	50	57	53.5	7	0.14
E44	63	69	66	6	0.17
E45	61	67	64	6	0.17
E46	53	60	56.5	7	0.14
E47	44	52	48	8	0.13
E49	50	55	52.5	5	0.20
E50	53	61	57	8	0.13
E51	43	51	47	8	0.13
H1	65	71	68	6	0.17
H2	62	69	65.5	7	0.14
H3	58	64	61	6	0.17
H4	53	60	56.5	7	0.14
H5	65	70	67.5	5	0.20
H6	66	71	68.5	5	0.20
H7	57	63	60	6	0.17
H8	45	49	47	4	0.25
H9	58	62	60	4	0.25
H10	55	60	57.5	5	0.20
J1	60	66	63	6	0.17
J2	55	62	58.5	7	0.14

Table XLII con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
J3	64	69	66.5	5	0.20
J4	65	71	68	6	0.17
J5	71	75	73	4	0.25
J6	70	75	72.5	5	0.20
J7	65	69	67	4	0.25
J8	71	75	73	4	0.25
J9	65	70	67.5	5	0.20
J10	71	76	73.5	5	0.20
J11	61	68	64.5	7	0.14
J12	65	71	68	6	0.17
J13	65	71	68	6	0.17
J14	65	72	68.5	7	0.14
J15	69	73	71	4	0.25

Table XLIII

Gold - conditions for first appearance of dendrites

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δ t
F11 B	36	38	37	2	0.50
F12 B	31	33	32	2	0.50
F13 C	22	23	22.5	1	1.00
F15 B	31	34	32.5	3	0.33
F16 A	32	34	33	2	0.50
F17 A	34	37	35.5	3	0.33
F17 B	34	36	35	2	0.50
F17 D	31	34	32.5	3	0.33
F18 B	31	33	32	2	0.50

Table XLIV

Gold - conditions for first appearance of hexagons

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δ t
F11 A	55	59	57	4	0.25
F11 B	57	61	59	4	0.25
F11 C	58	62	60	4	0.25
F11 D	58	62	60	4	0.25
F12 A	52	59	55.5	7	0.14
F12 B	52	58	55	6	0.17
F12 C	50	55	52.5	5	0.20
F12 D	50	56	53	6	0.17
F13 A	62	73	67.5	11	0.09
F13 B	62	70	66	8	0.13
F13 C	65	72	68.5	7	0.14
F14 A	77	81	79	4	0.25
F14 B	74	78	76	4	0.25
F14 C	78	83	80.5	5	0.20
F14 D	77	82	79.5	5	0.20
F15 A	62	71	66.5	9	0.11
F15 B	70	78	74	8	0.13
F15 C	77	83	80	6	0.17
F15 D	76	81	78.5	5	0.20
F16 A	80	84	82	4	0.25
F16 B	78	83	80.5	5	0.20
F16 C	71	77	74	6	0.17
F16 D	75	80	77.5	5	0.20
F17 A	80	85	82.5	5	0.20

Table XLIV con't

Run No.	Outlet Temp ^{o}C	Inlet Temp ^{o}C	Ave. Temp ^{o}C	Δt C^{o}	$1/\Delta t$
F17 B	74	80	77	6	0.17
F17 C	82	86	84	4	0.25
F17 D	80	85	82.5	5	0.20
F18 A	78	85	81.5	7	0.14
F18 B	77	85	81	8	0.13
F18 C	78	84	81	6	0.17
F18 D	80	85	82.5	5	0.20

Table XLV

Gold - conditions for first appearance of rods

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
F11 B	46	49	47.5	3	0.33
F11 C	45	48	46.5	3	0.33
F11 D	47	49	48	2	0.50
F12 A	48	52	50	4	0.25
F12 B	48	52	50	4	0.25
F12 C	40	43	41.5	3	0.33
F13 A	20	21	20.5	1	1.00
F13 B	32	35	33.5	3	0.33
F13 C	33	37	35	4	0.25
F14 A	47	51	49	4	0.25
F14 C	44	47	45.5	3	0.33
F14 D	51	55	53	4	0.25
F15 A	42	45	43.5	3	0.33
F15 B	43	47	45	4	0.25
F15 C	40	42	41	2	0.50
F15 D	31	33	32	2	0.50
F16 A	46	50	48	4	0.25
F16 C	28	30	29	2	0.50
F16 D	39	43	41	4	0.25
F17 A	45	48	46.5	3	0.33
F17 B	44	47	45.5	3	0.33
F17 C	52	57	54.5	5	0.20
F17 D	52	56	54	4	0.25
F18 A	45	48	46.5	3	0.33

Table XLV con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δ t
F18 B	46	51	48.5	5	0.20
F18 C	51	55	53	4	0.25
F18 D	50	55	52.5	5	0.20

Table XLVI

Gold - conditions for first appearance of squares

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δ t
F11 A	33	34	33.5	1	1.00
F11 C	35	37	36	2	0.50
F11 D	35	37	36	2	0.50
F12 C	38	40	39	2	0.50
F12 D	31	33	32	2	0.50
F13 A	36	40	38	4	0.25
F13 C	31	33	32	2	0.50
F14 B	32	35	33.5	3	0.33
F14 D	29	33	31	4	0.25
F16 B	33	35	34	2	0.50
F17 A	39	42	40.5	3	0.33
F17 C	35	38	36.5	3	0.33
F18 A	37	39	38	2	0.50
F18 B	38	40	39	2	0.50

Table XLVII

Gold - conditions for first appearance of trapezoids

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	1/Δt
F11 A	46	49	47.5	3	0.33
F11 C	48	50	49	2	0.50
F11 D	45	48	46.5	3	0.33
F12 A	48	52	50	4	0.25
F12 B	38	41	39.5	3	0.33
F12 D	45	49	47	4	0.25
F13 A	21	22	21.5	1	1.00
F13 B	44	48	46	4	0.25
F13 C	49	57	53	8	0.13
F14 A	51	56	53.5	5	0.20
F14 B	51	55	53	4	0.25
F14 C	51	56	53.5	5	0.20
F14 D	51	56	53.5	5	0.20
F15 C	55	61	58	6	0.17
F15 D	50	54	52	4	0.25
F16 A	56	61	58.5	5	0.20
F16 B	50	50	52	4	0.25
F16 D	52	56	54	4	0.25
F17 A	54	61	57.5	7	0.14
F17 B	47	54	50.5	7	0.14
F17 C	48	52	50	4	0.25
F17 D	46	52	49	6	0.17
F18 A	54	60	57	6	0.17
F18 B	51	57	54	6	0.17
F18 C	55	59	57	4	0.25
F18 D	52	56	54	4	0.25

Table XLVIII

Gold - conditions for first appearance of triangles

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
F11 A	55	59	57	4	0.25
F11 B	57	61	59	4	0.25
F11 C	58	62	60	4	0.25
F11 D	58	62	60	4	0.25
F12 A	52	59	55.5	7	0.14
F12 B	52	58	55	6	0.17
F12 C	50	55	52.5	5	0.20
F12 D	50	56	53	6	0.17
F13 A	62	73	67.5	11	0.09
F13 B	62	70	66	8	0.13
F13 C	65	72	68.5	7	0.14
F14 A	77	81	79	4	0.25
F14 B	74	78	76	4	0.25
F14 C	78	83	80.5	5	0.20
F14 D	77	82	79.5	5	0.20
F15 A	54	62	58	8	0.13
F15 B	70	78	74	8	0.13
F15 C	67	73	70	6	0.17
F15 D	76	81	78.5	5	0.20
F16 A	80	84	82	4	0.25
F16 B	78	83	80.5	5	0.20
F16 C	71	77	74	6	0.17
F16 D	75	80	77.5	5	0.20
F17 A	80	85	82.5	5	0.20

Table XLVIII con't

Run No.	Outlet Temp °C	Inlet Temp °C	Ave. Temp °C	Δt C°	$1/\Delta t$
F17 B	74	80	77	6	0.17
F17 C	82	86	84	4	0.25
F17 D	80	85	82.5	5	0.20
F18 A	78	85	81.5	7	0.14
F18 B	77	85	81	8	0.13
F18 C	78	82	80	4	0.25
F18 D	80	85	82.5	5	0.20

APPENDIX B

Graphical Presentation of Data

in

Tables of Appendix A

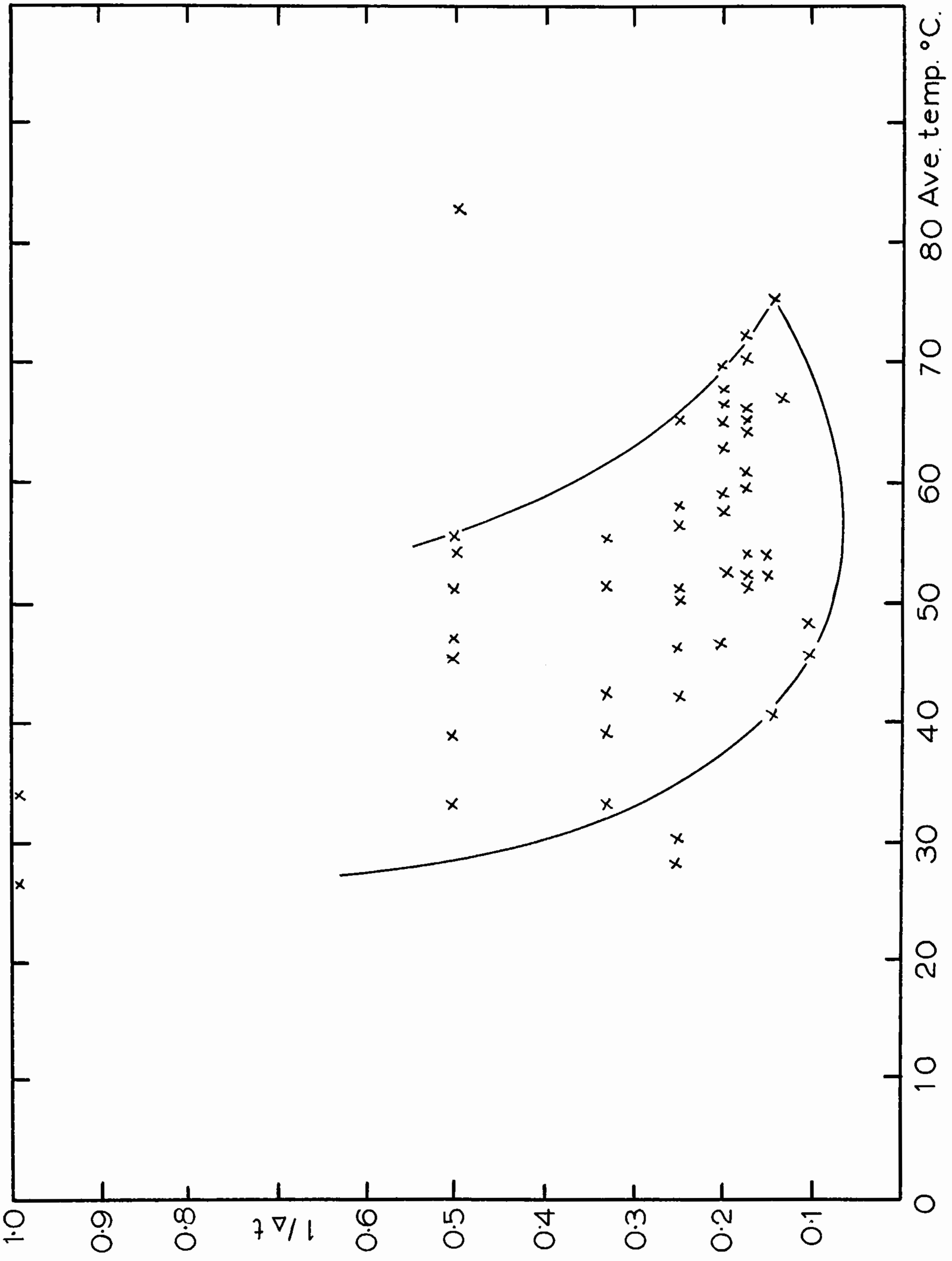


FIG. 27

Copper. Conditions for first appearance of bent wires.

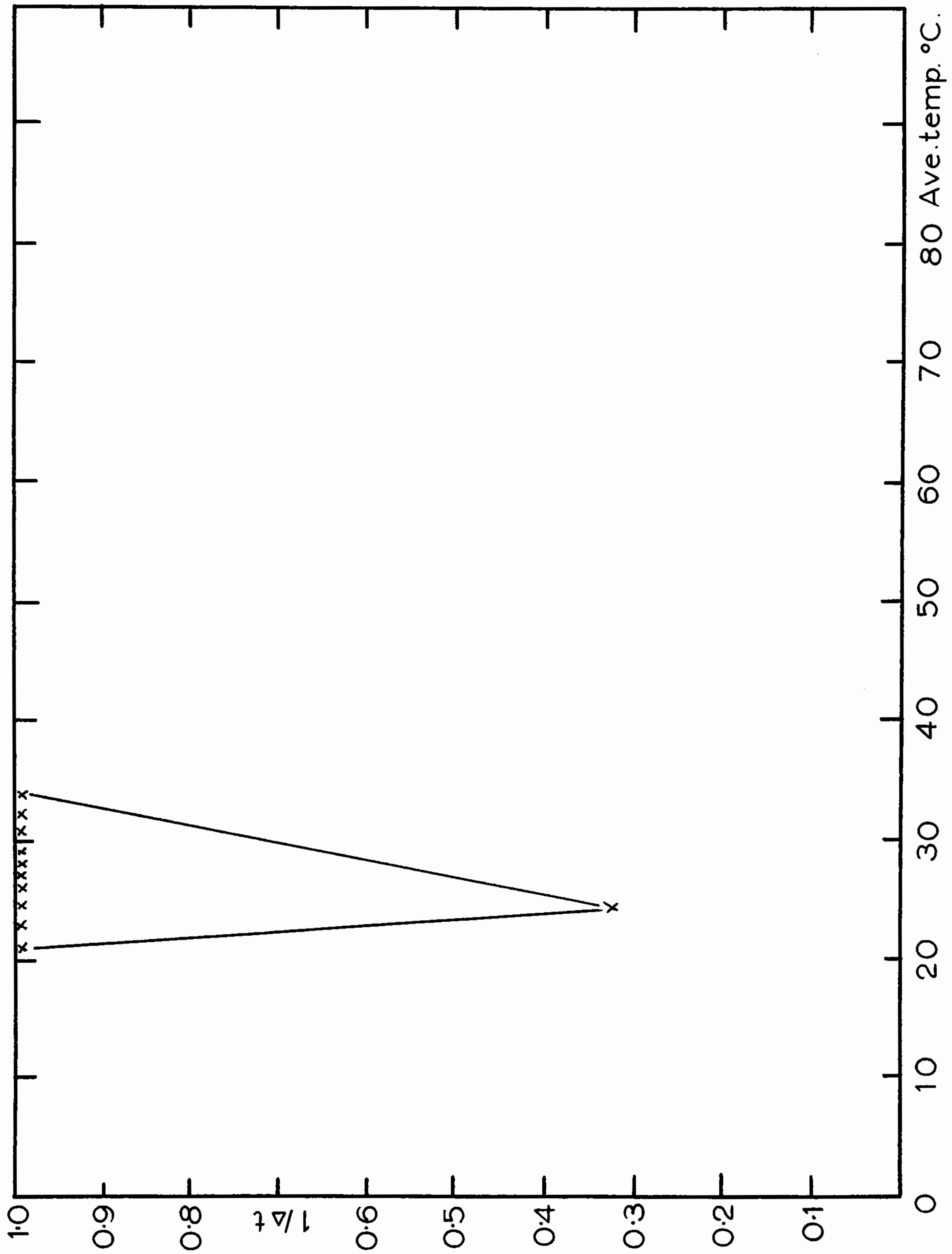


FIG. 28

Copper. Conditions for first appearance of dendrites.

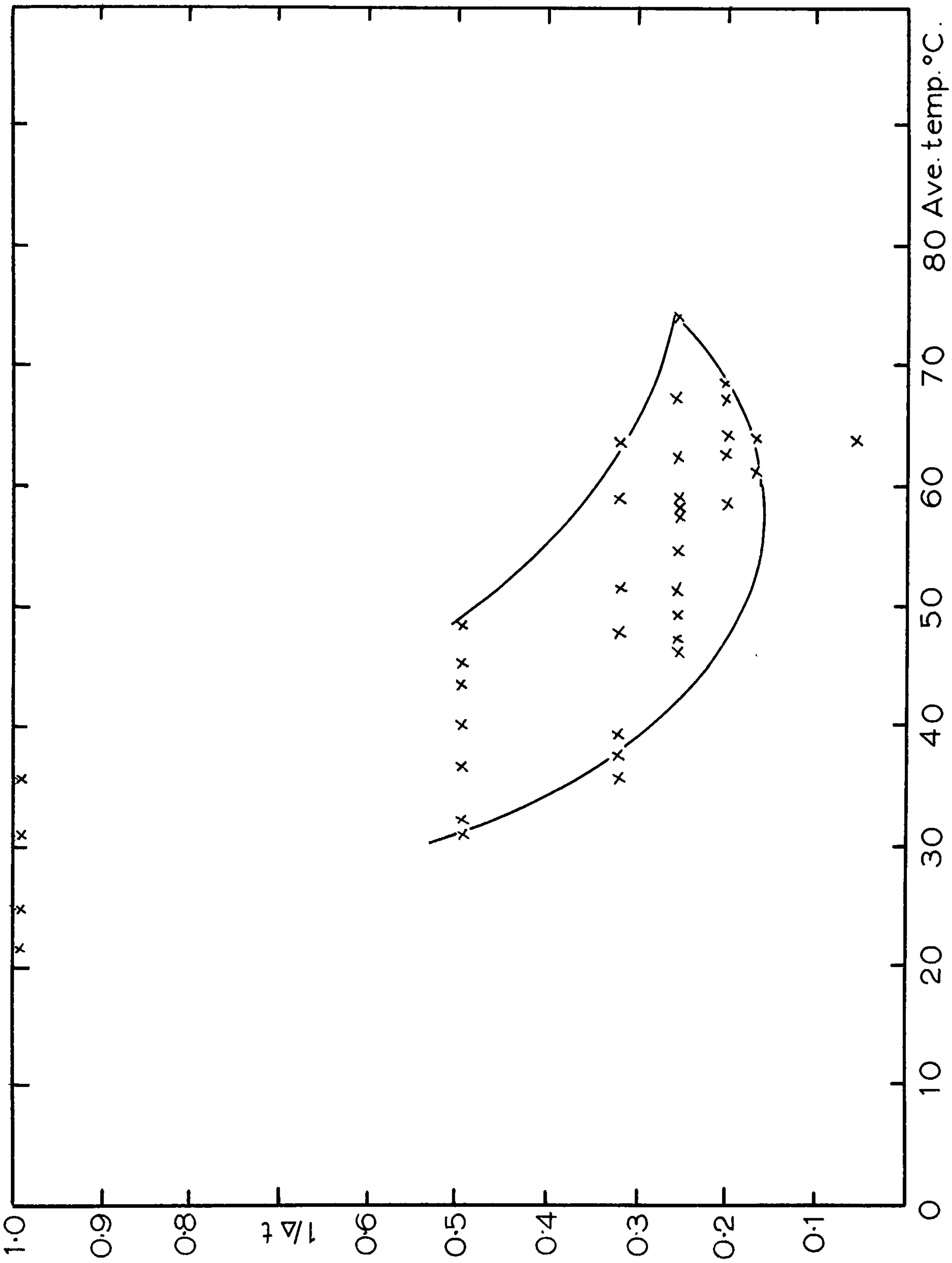


FIG. 29

Copper. Conditions for first appearance of diamonds.

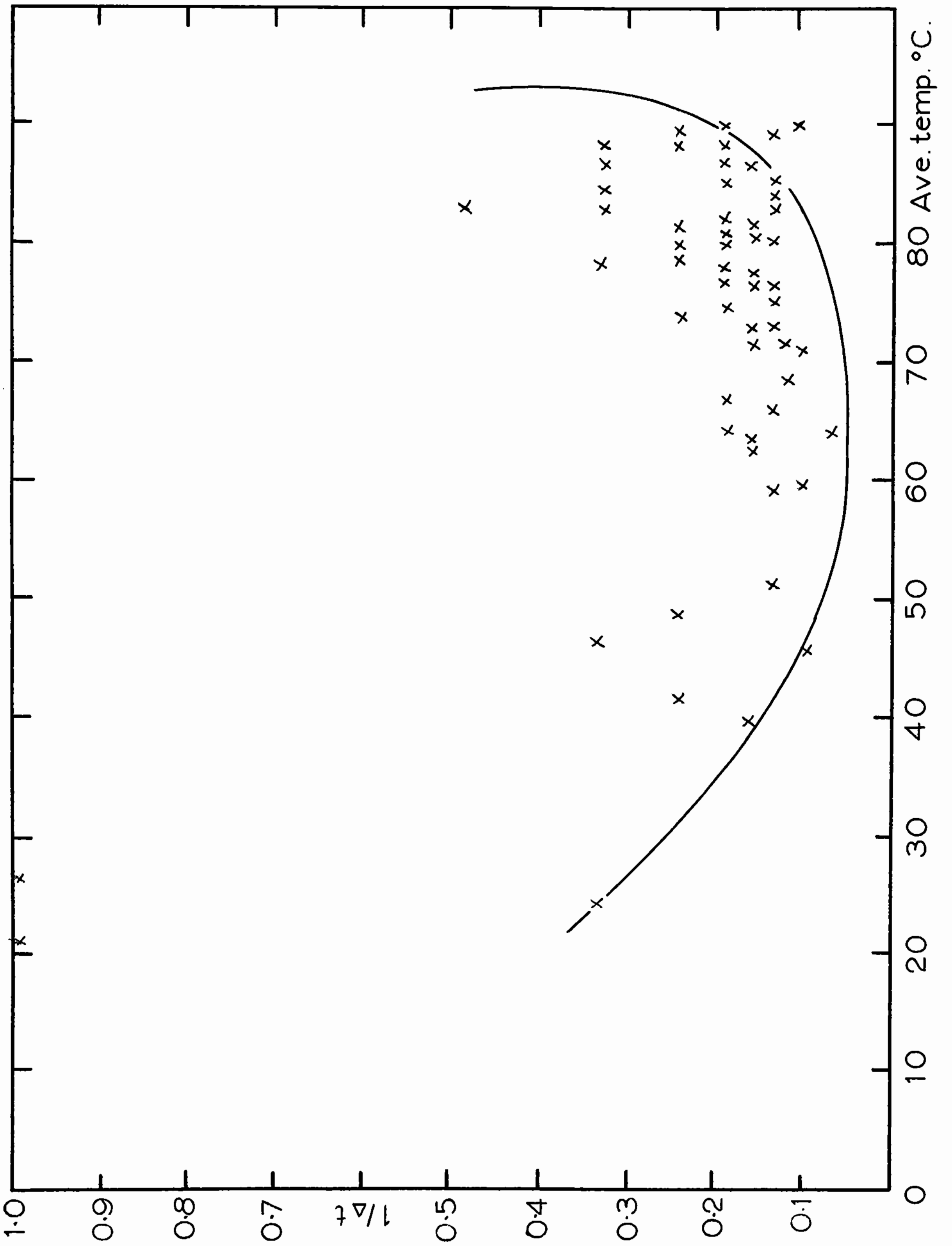


FIG. 30

Copper. Conditions for first appearance of hexagons.

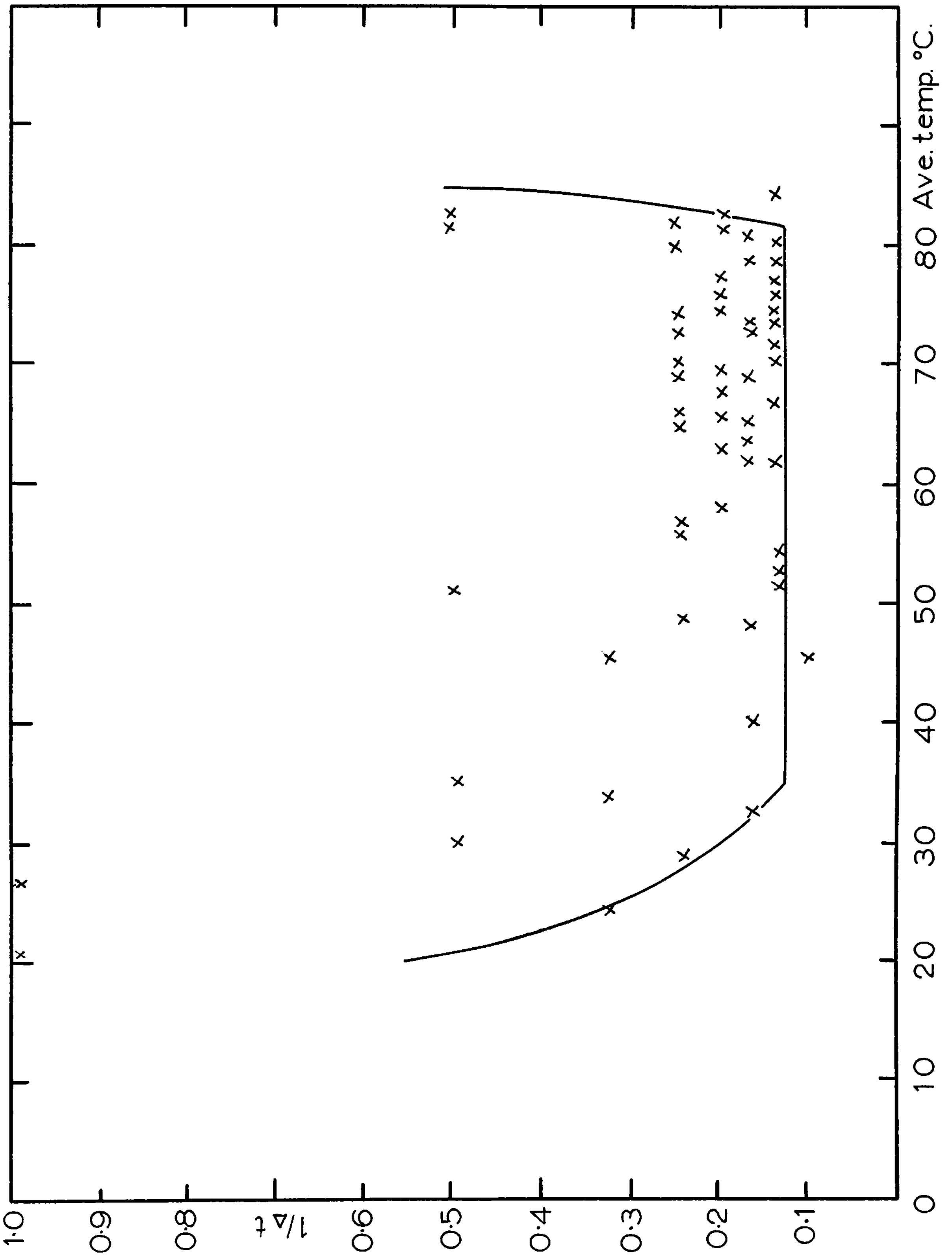


FIG. 31

Copper. Conditions for first appearance of needles.

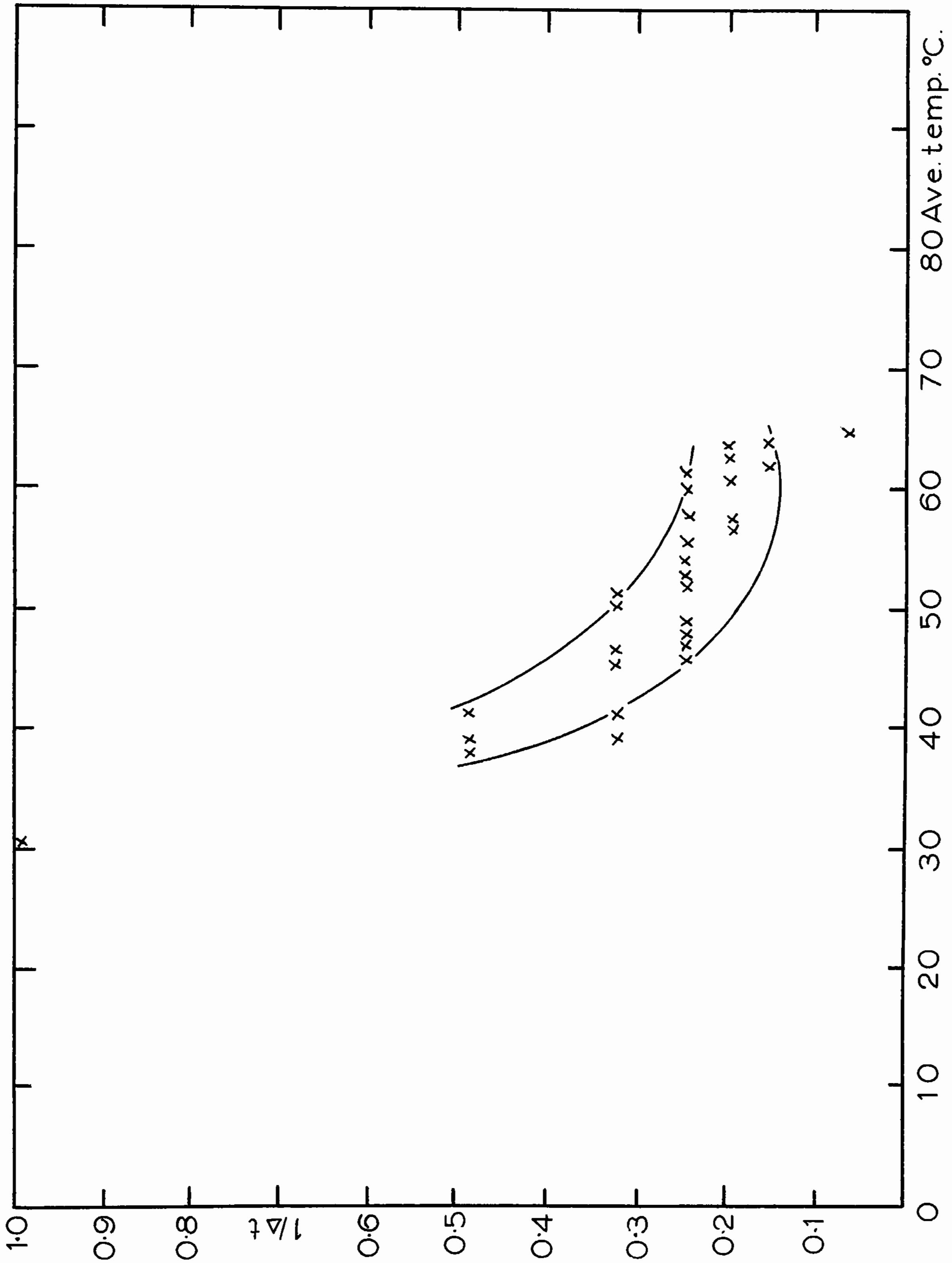


FIG. 32

Copper. Conditions for first appearance of octagons.

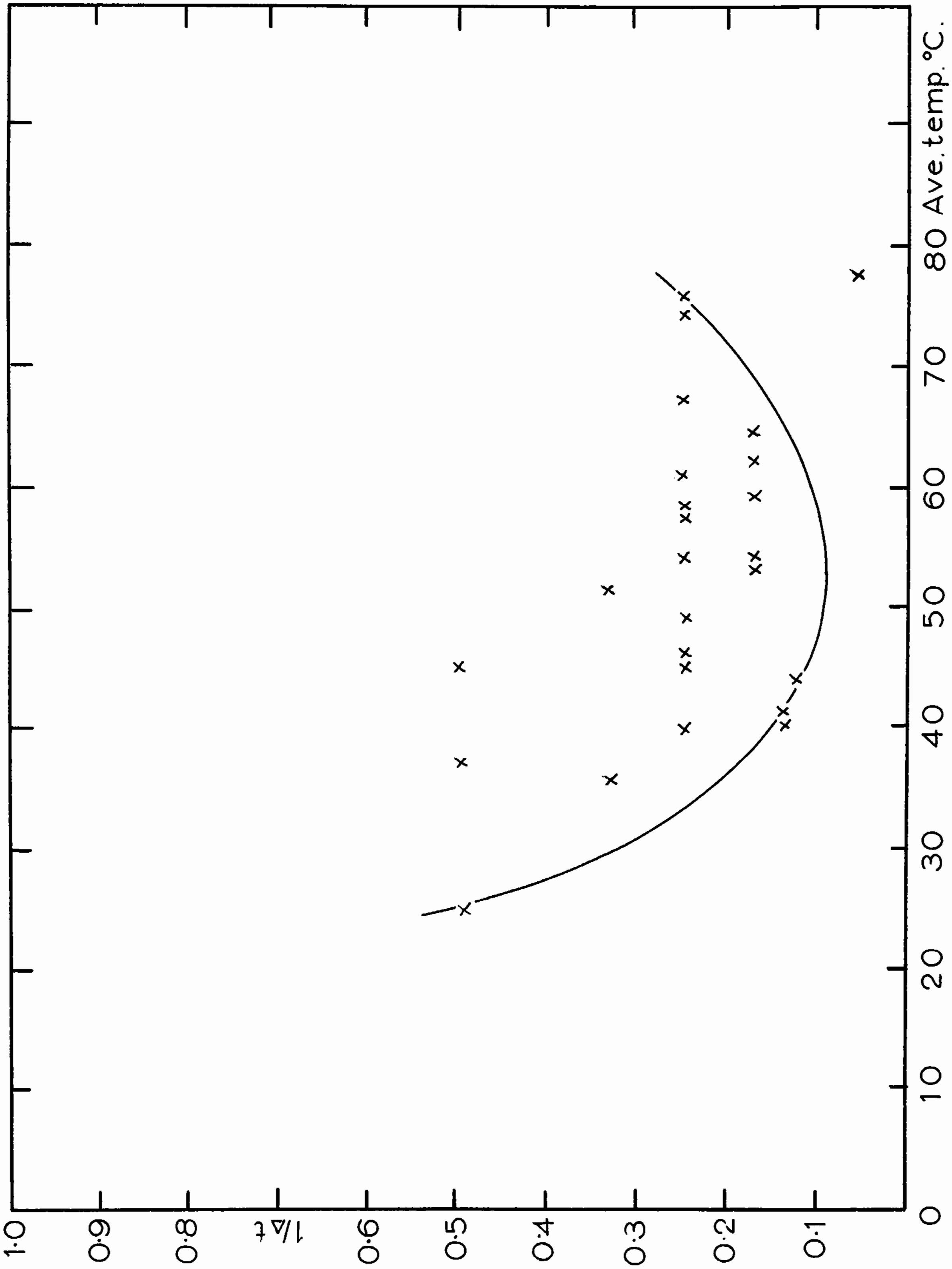


FIG. 33

Copper. Conditions for first appearance of pentagons.

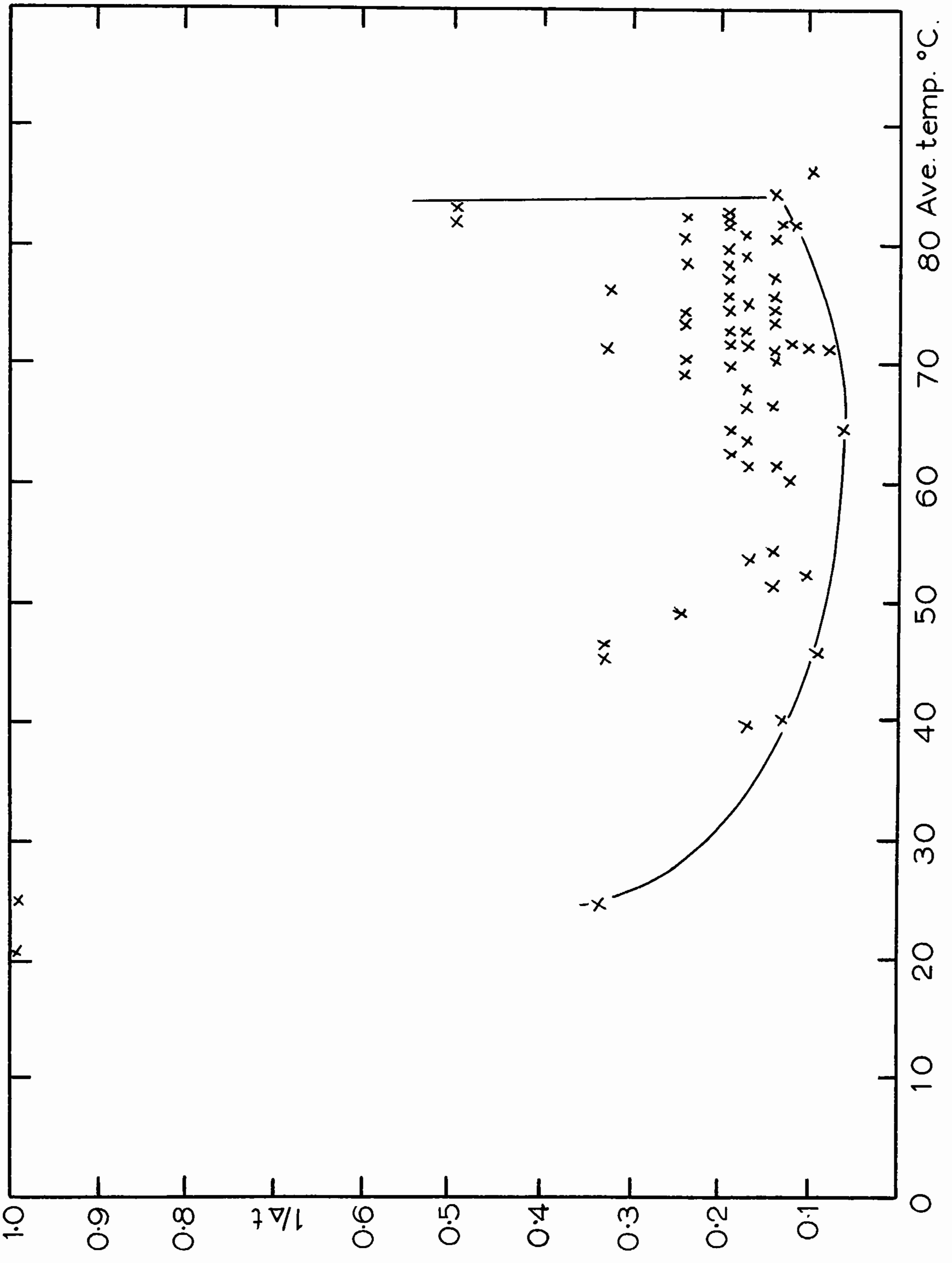


FIG. 34

Copper. Conditions for first appearance of rods.

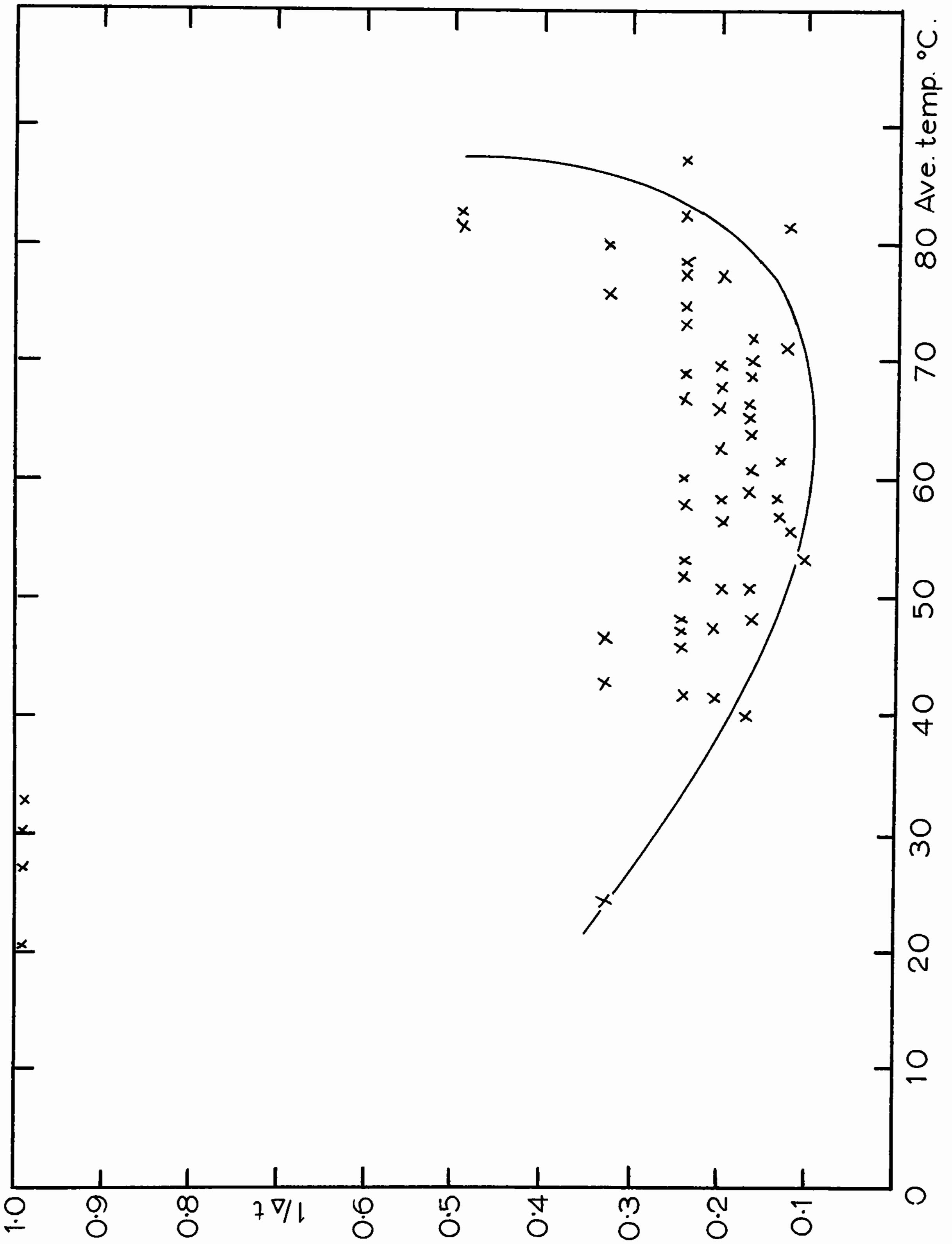


FIG. 35

Copper. Conditions for first appearance of squares.

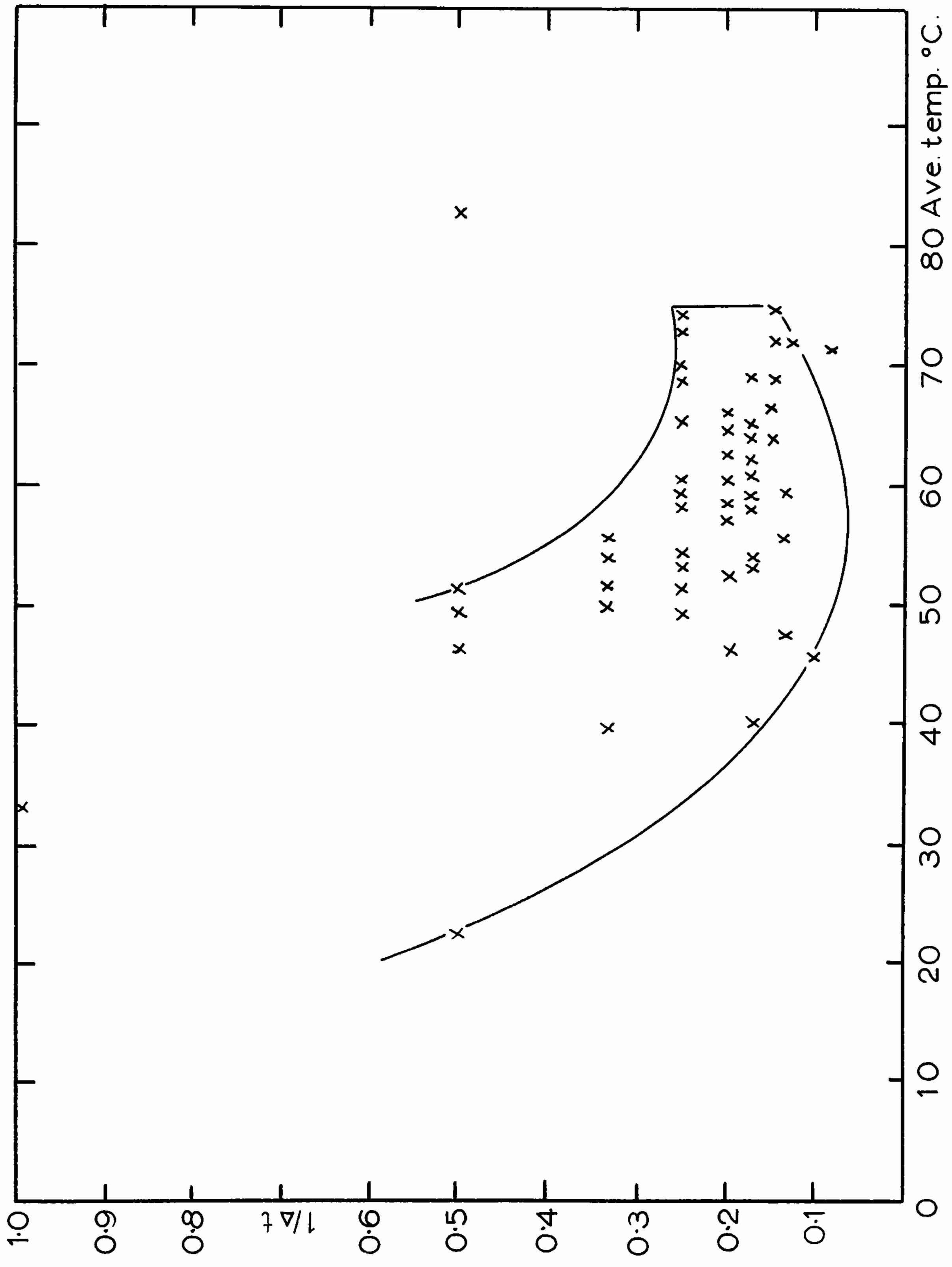


FIG. 36

Copper. Conditions for first appearance of trapezoids.

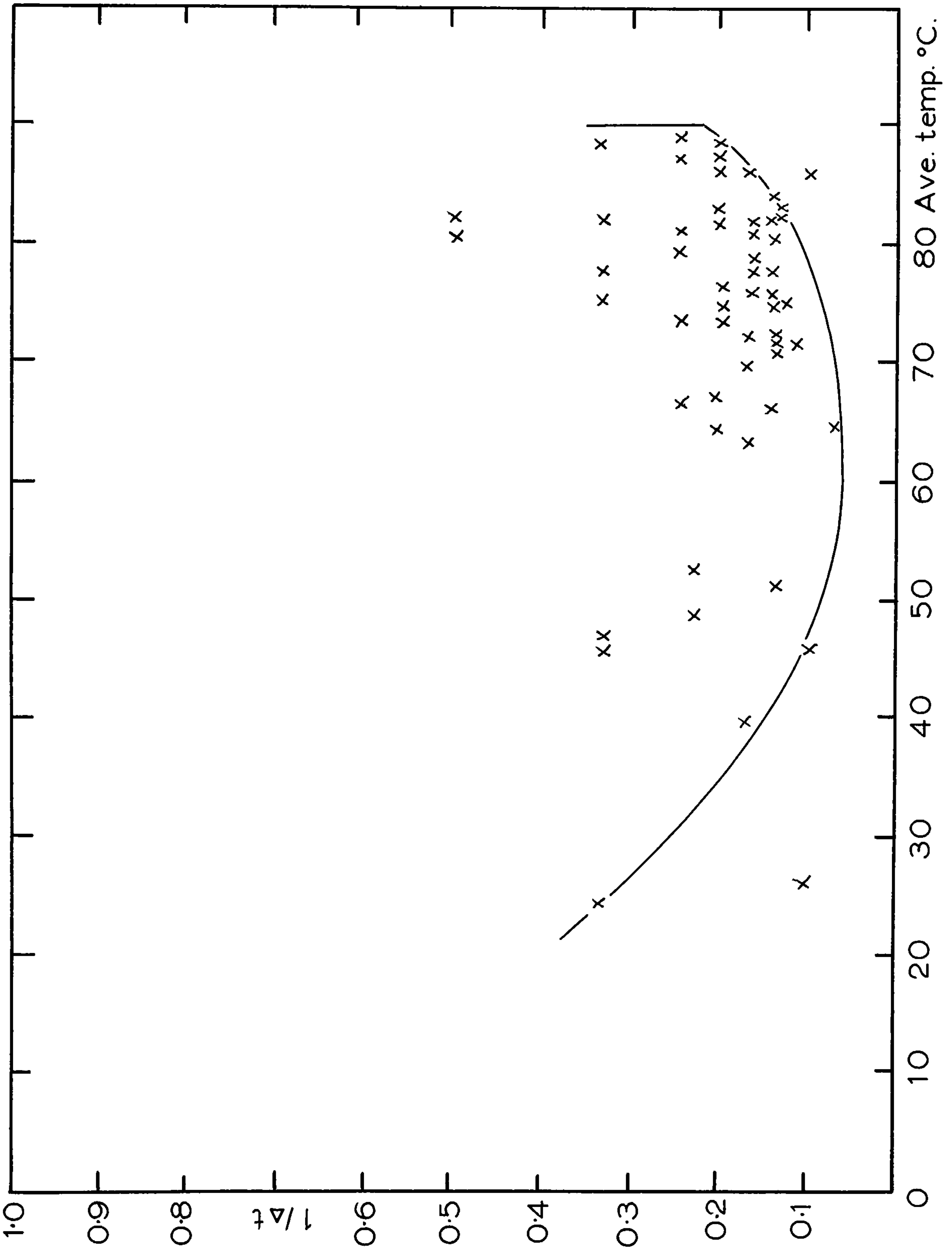


FIG. 37

Copper. Conditions for first appearance of triangles.

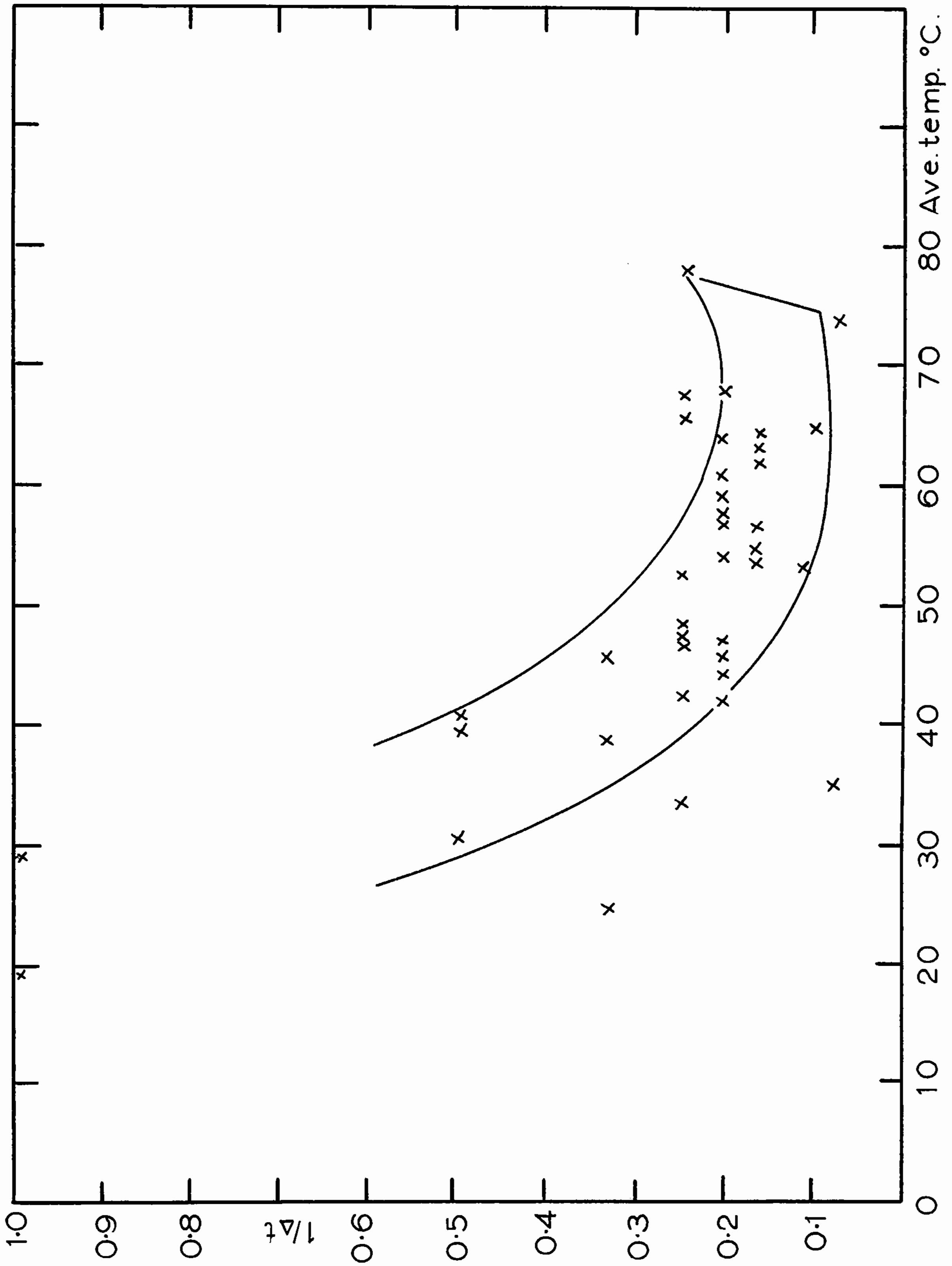


FIG. 38

Copper. Conditions for first appearance of truncated diamonds.

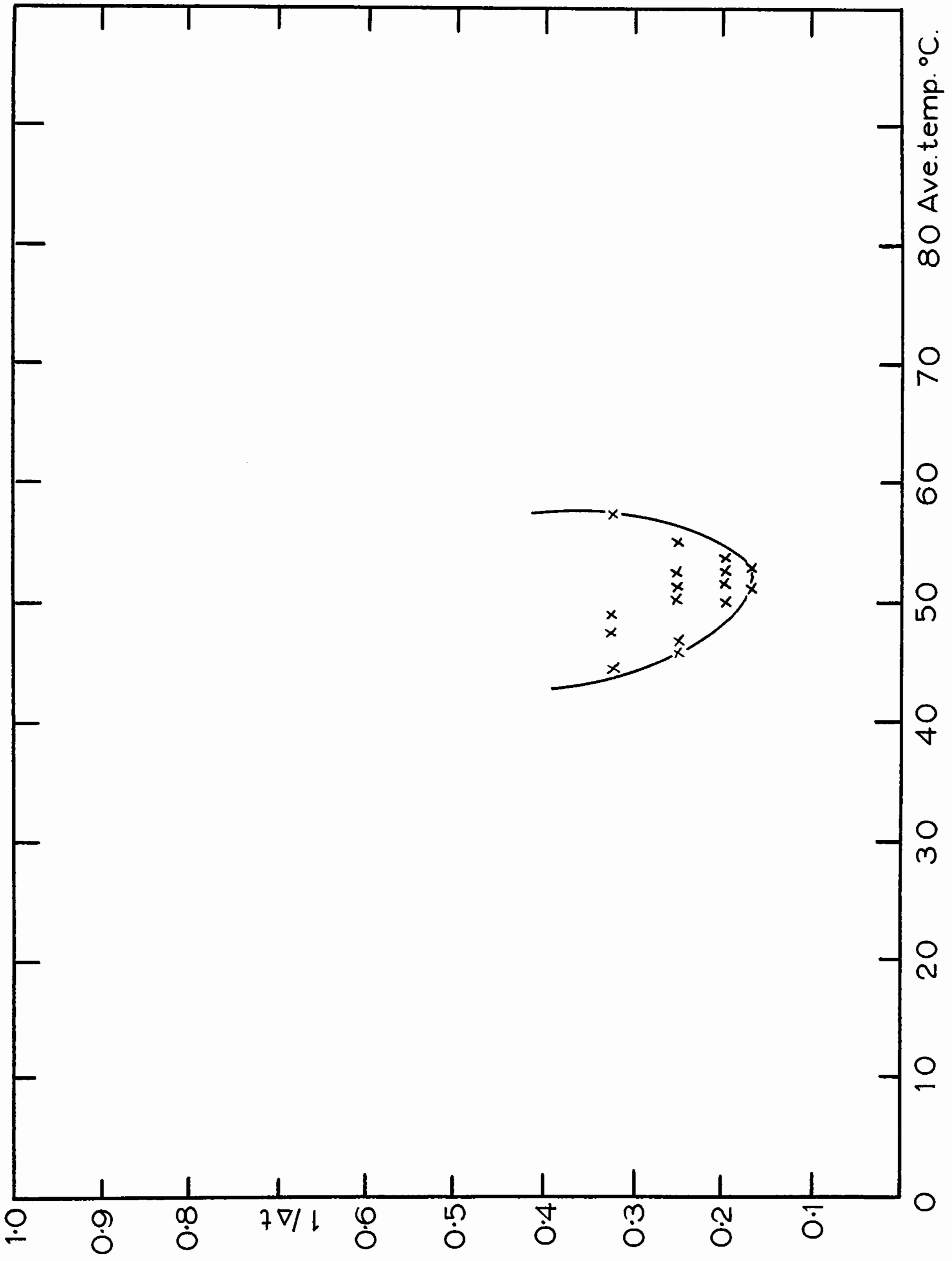


FIG. 39

Silver. Conditions for first appearance of bent wires.

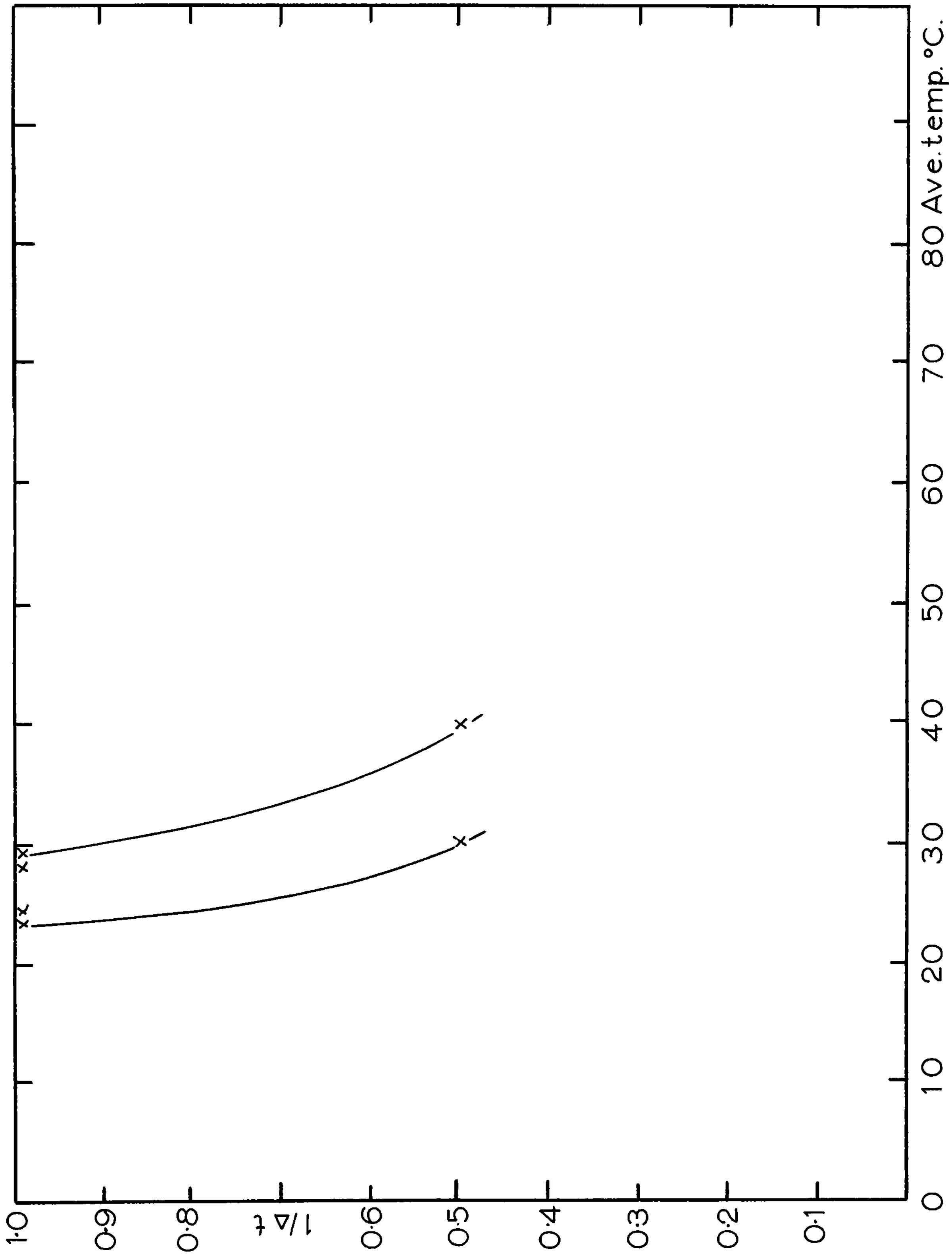


FIG. 40

Silver. Conditions for first appearance of dendrites.

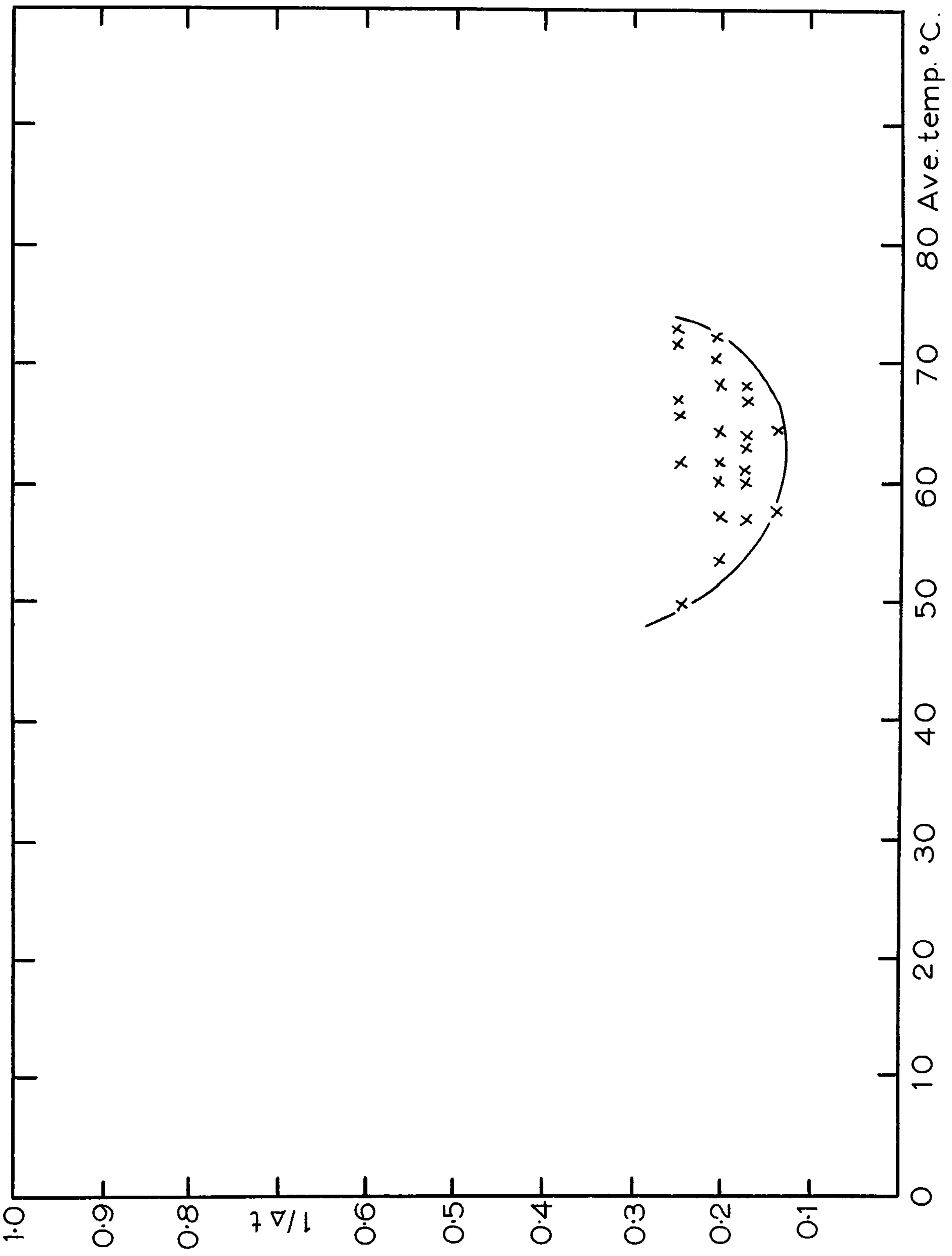


FIG. 41

Silver. Conditions for first appearance of diamonds.

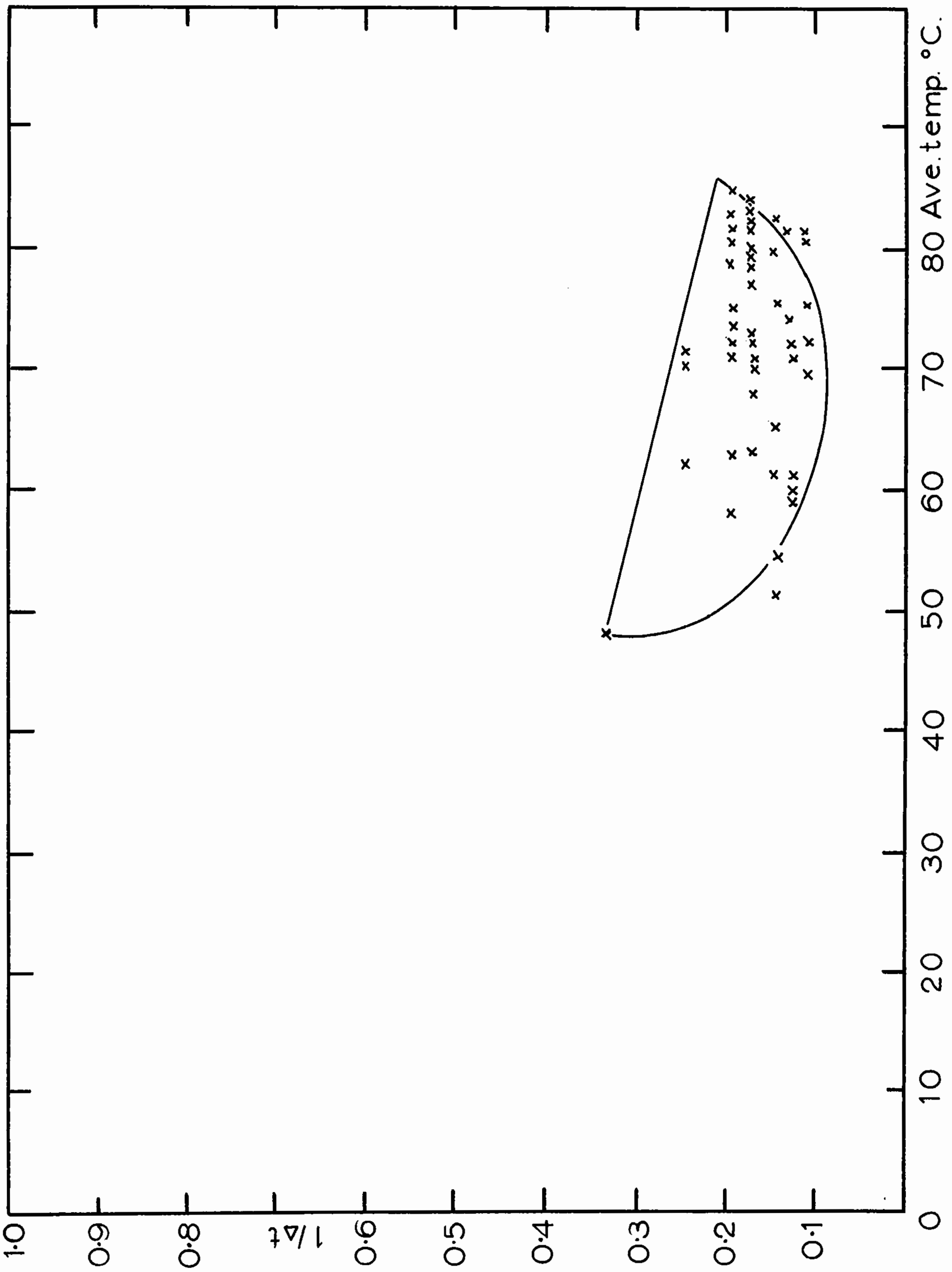


FIG 42

Silver. Conditions for first appearance of hexagons.

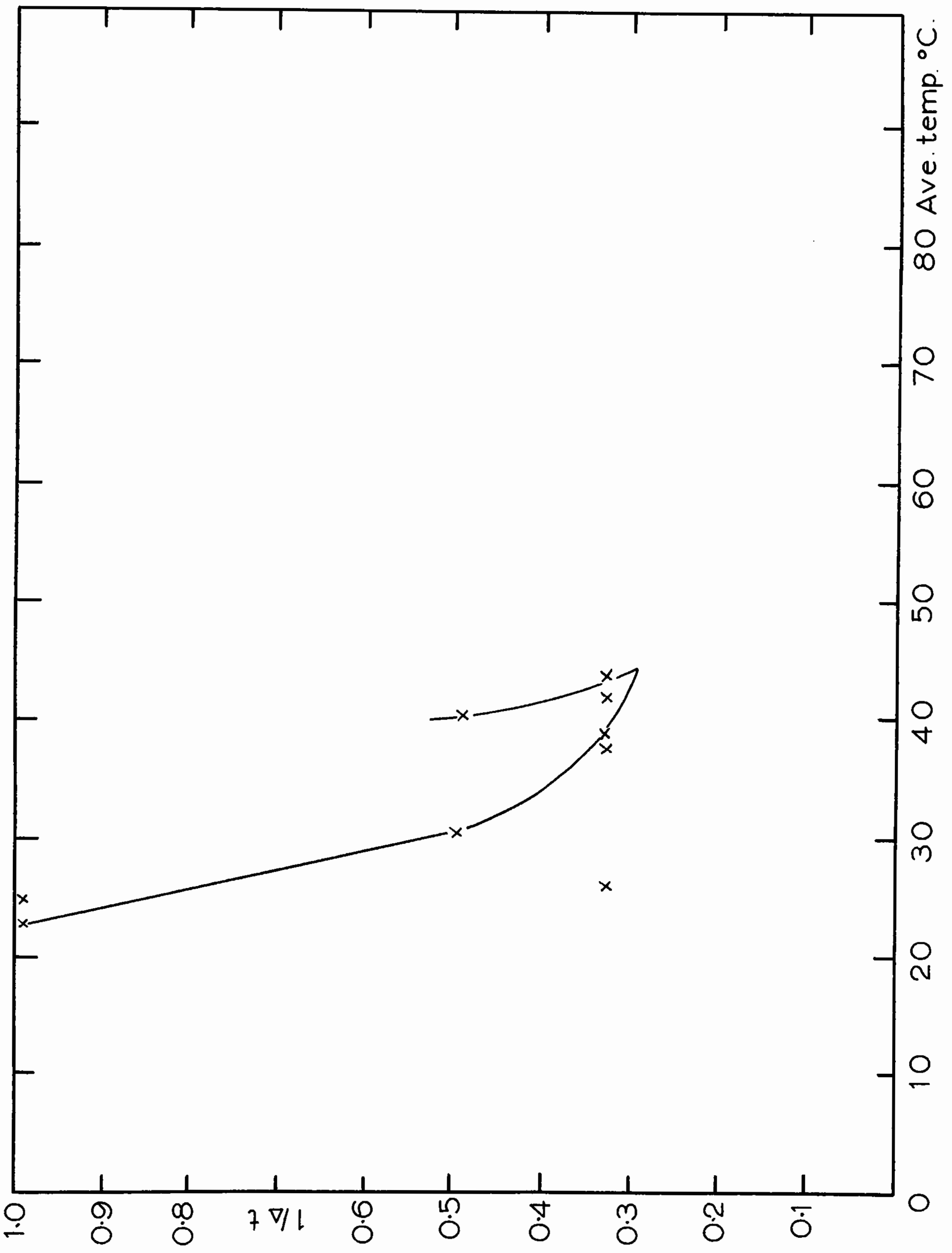


FIG. 43

Silver. Conditions for first appearance of needles.

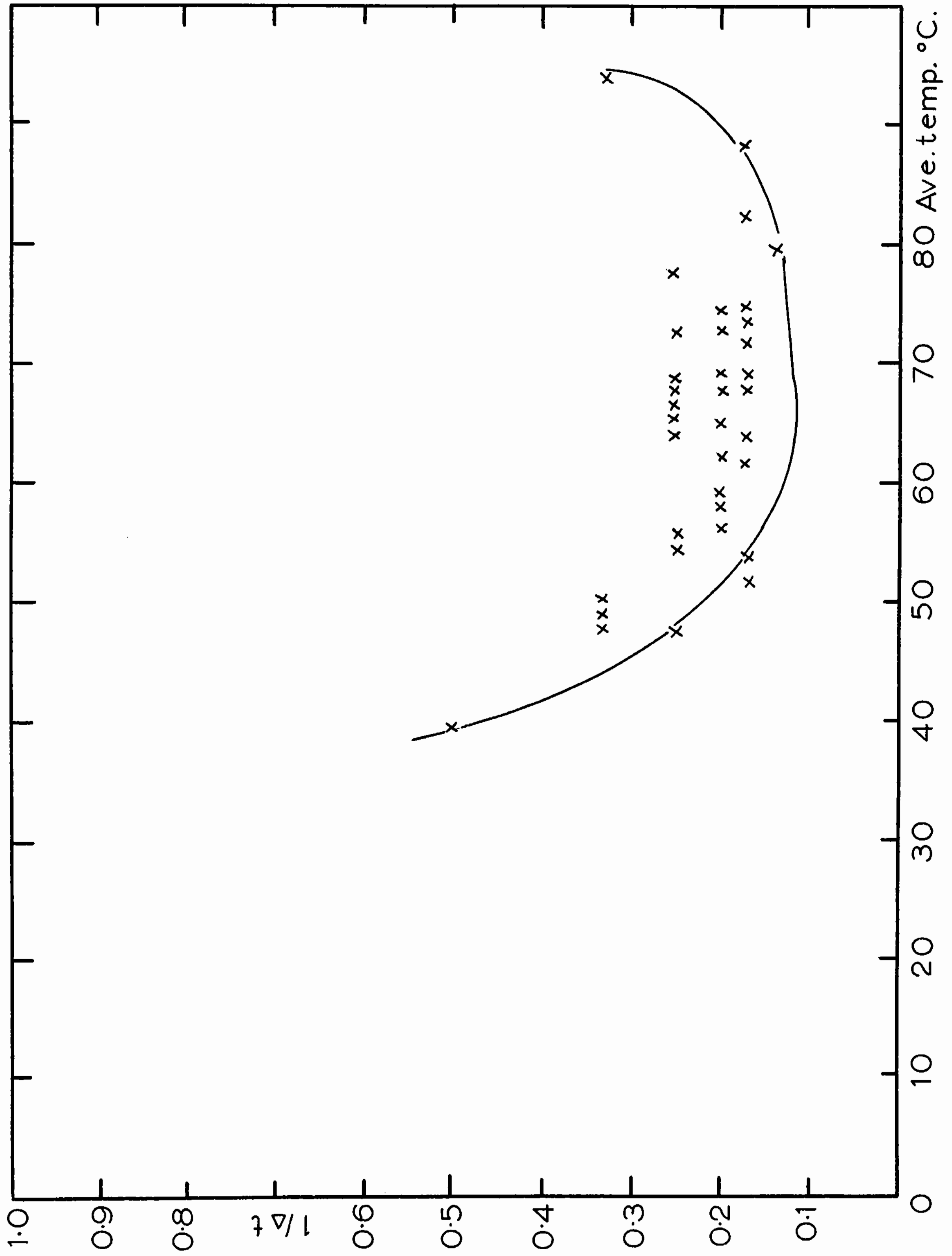


FIG. 44

Silver. Conditions for first appearance of octagons.

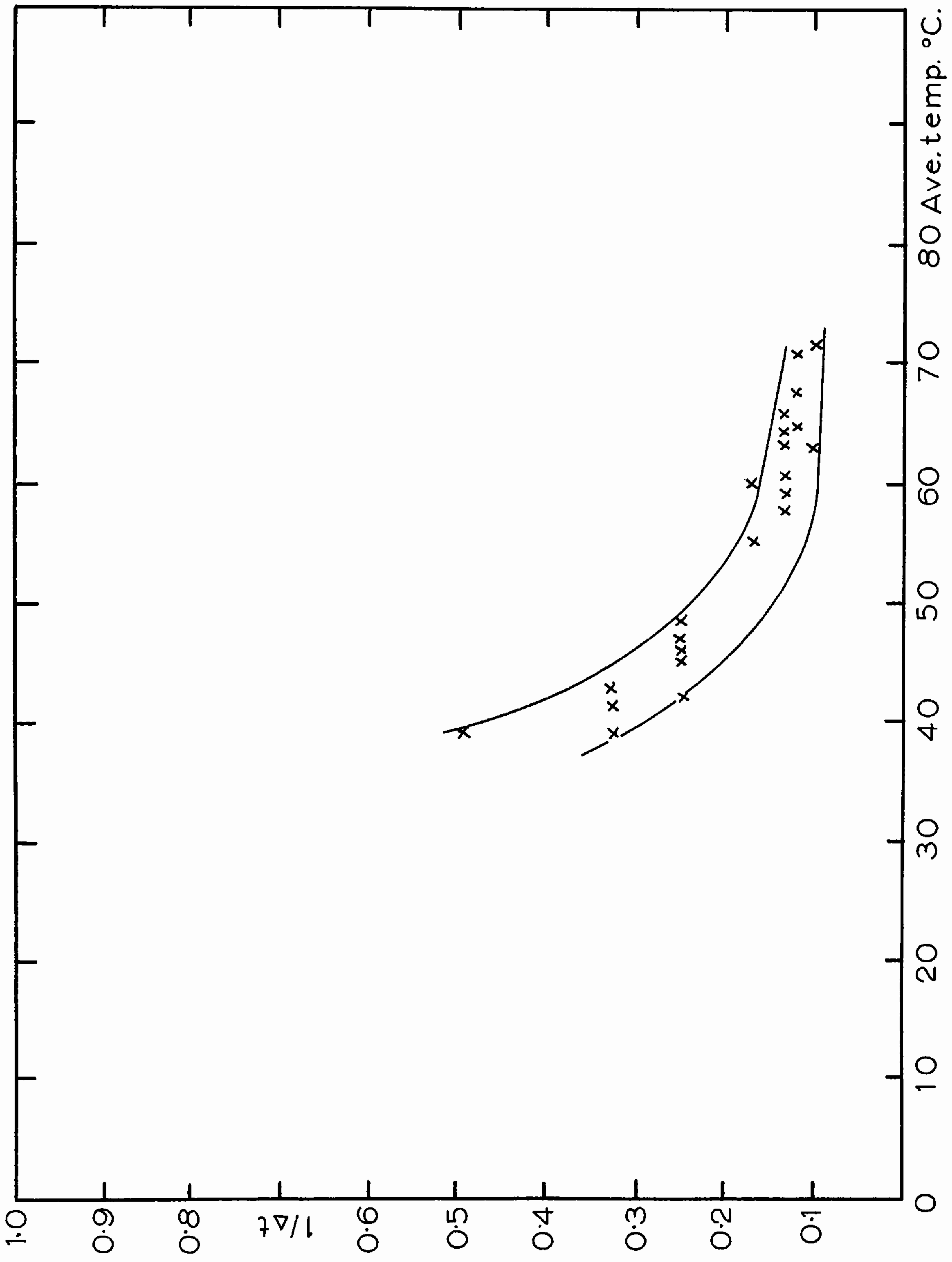


FIG. 45

Silver. Conditions for first appearance of pentagons.

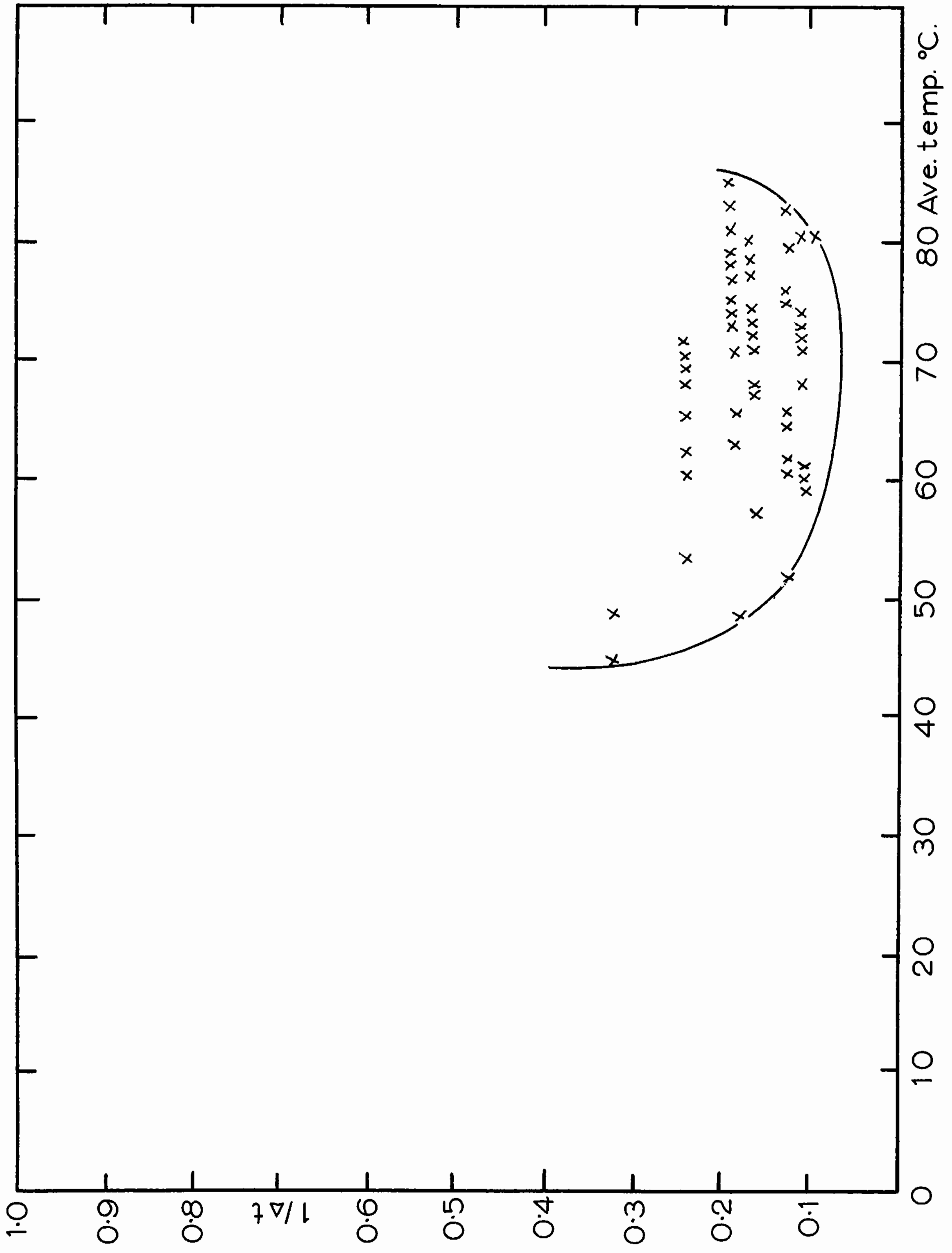


FIG. 46

Silver. Conditions for first appearance of rods.

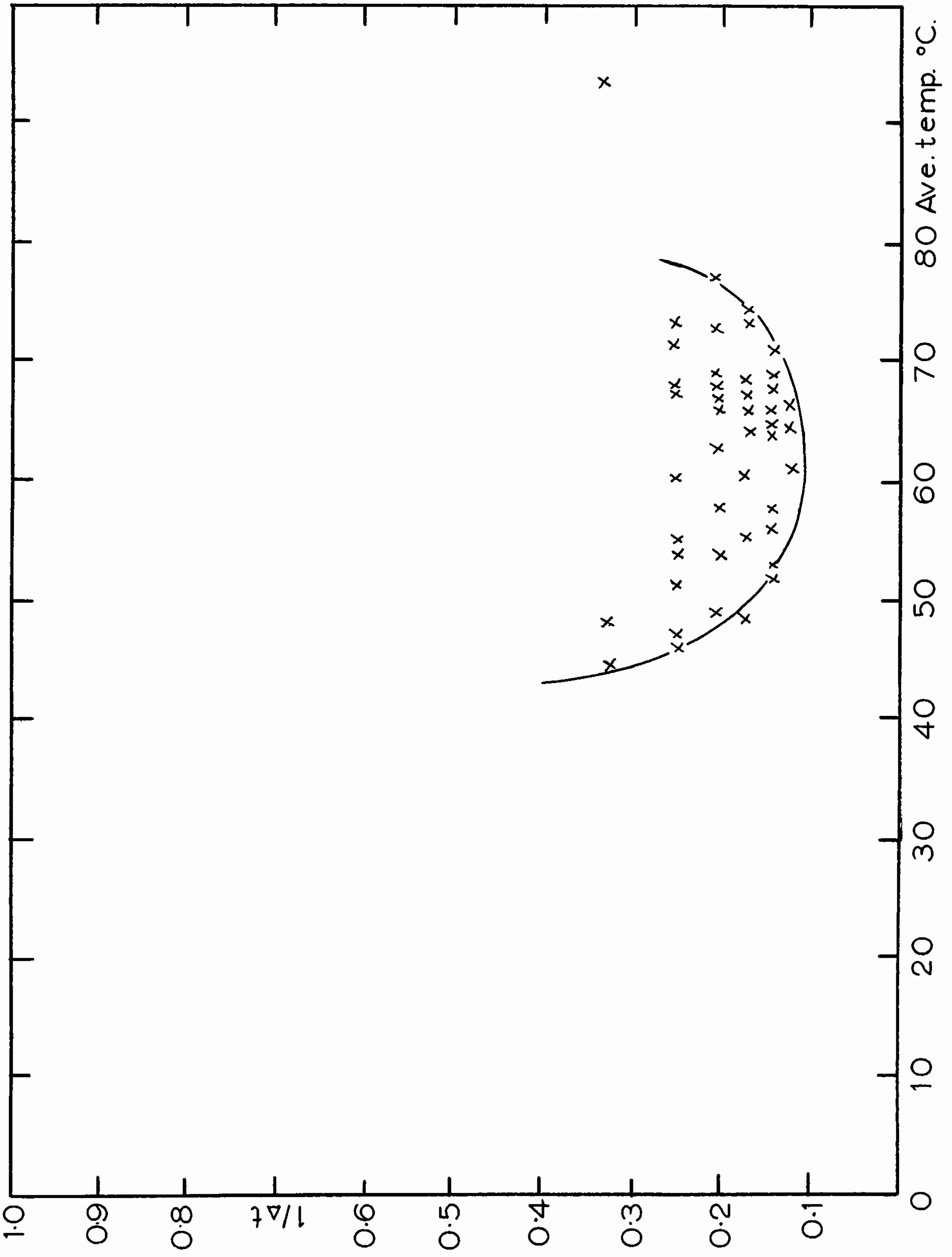


FIG. 47

Silver. Conditions for first appearance of squares.

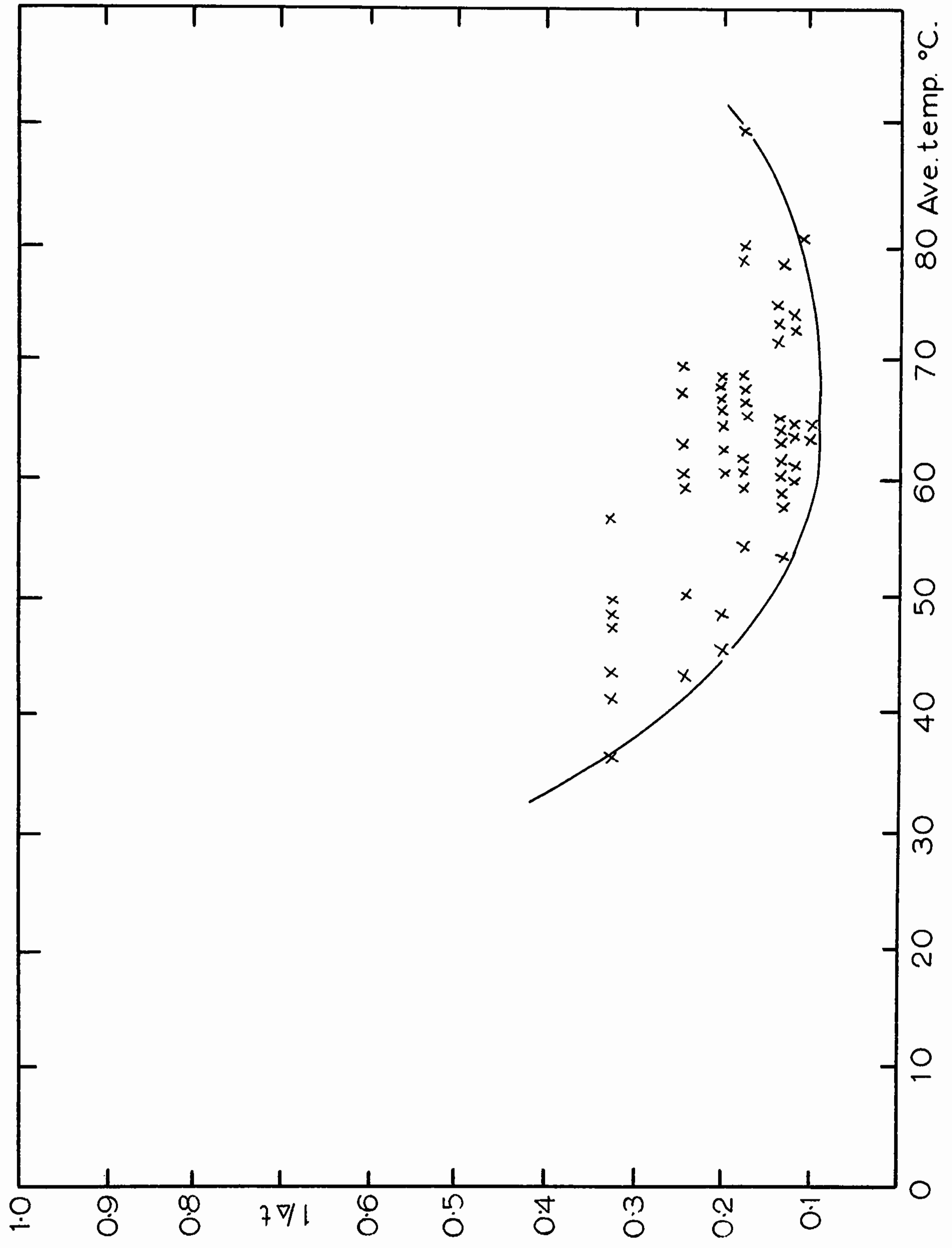


FIG. 48

Silver. Conditions for first appearance of trapezoids.

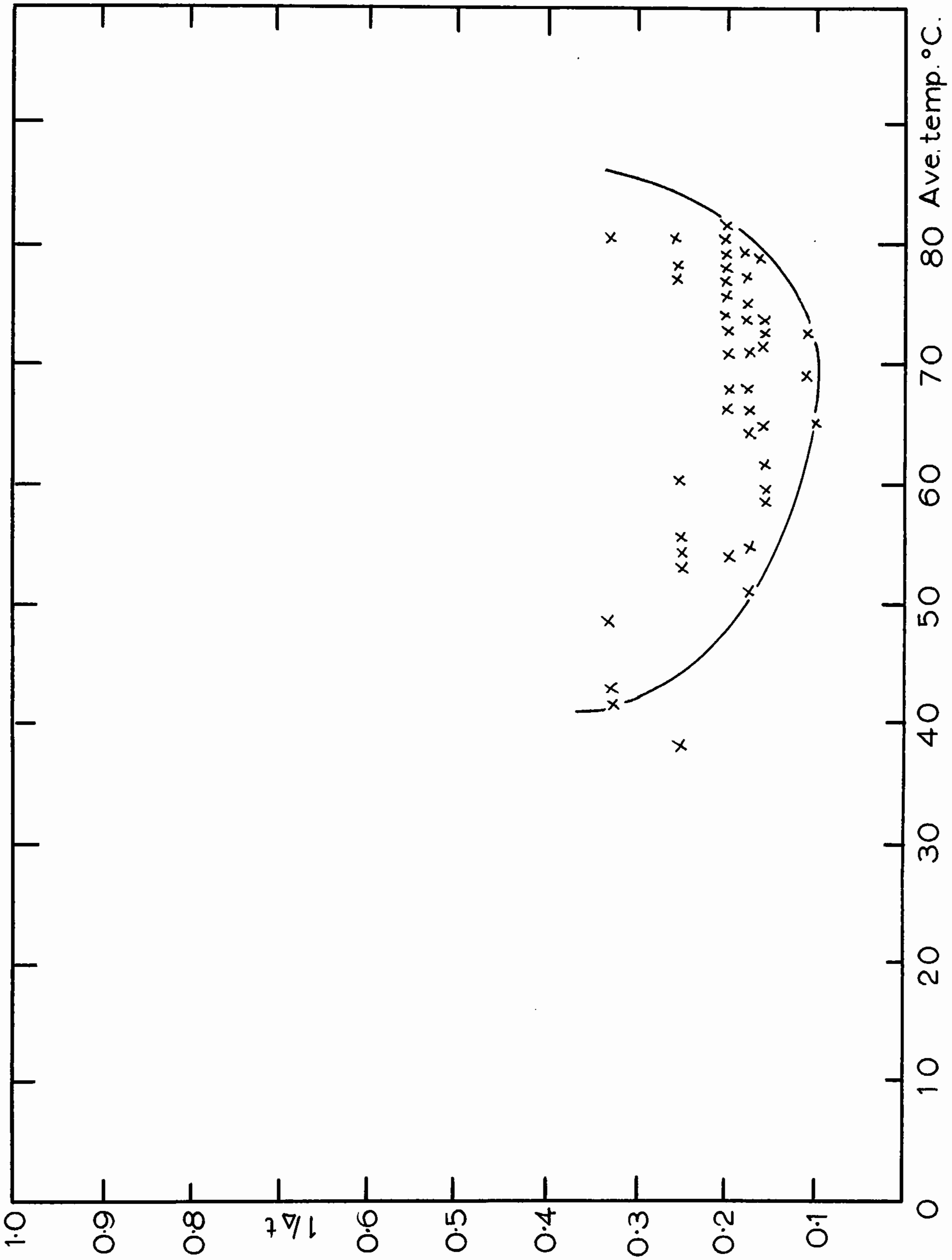


FIG. 49

Silver. Conditions for first appearance of triangles.

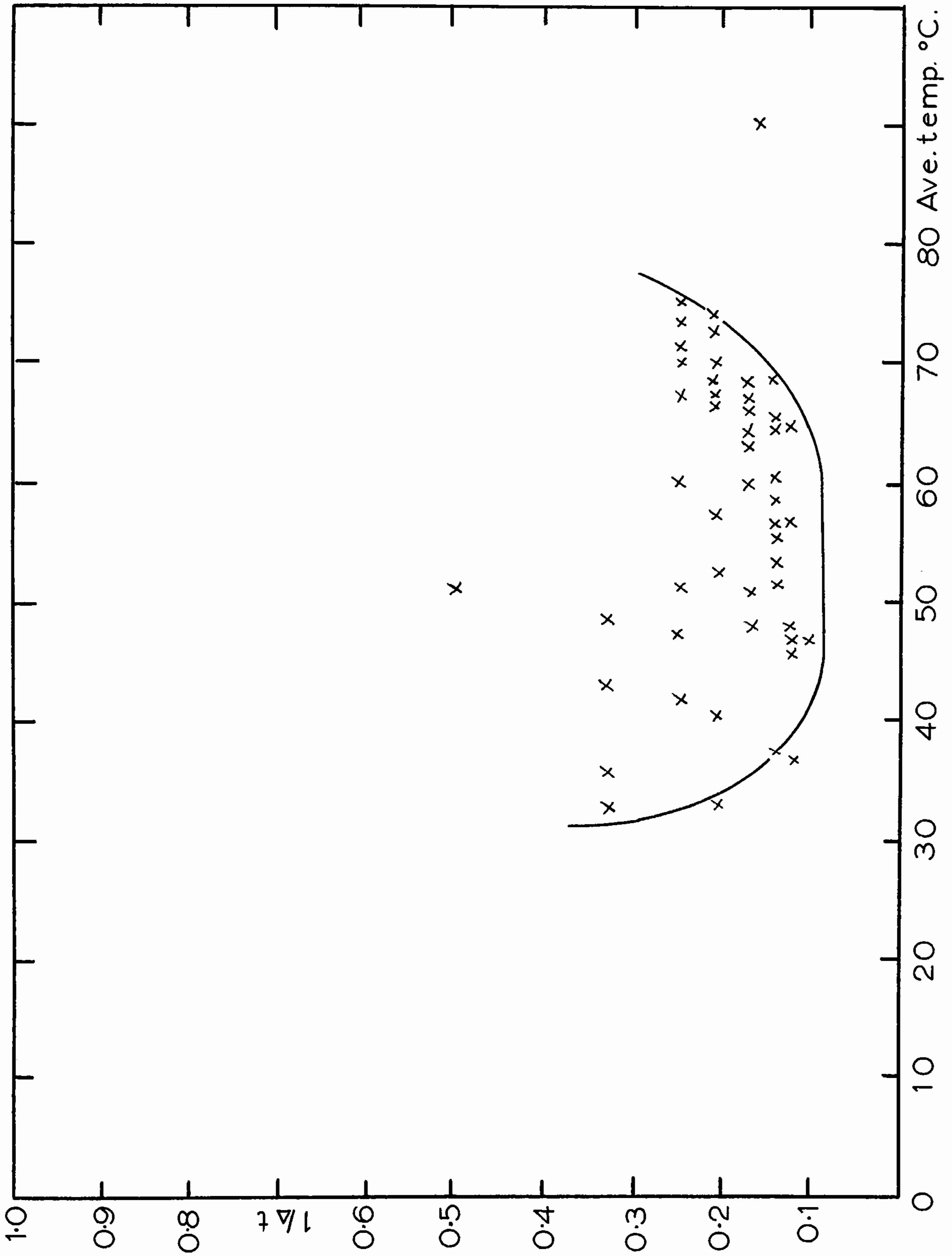


FIG. 50

Silver. Conditions for first appearance of truncated diamonds.

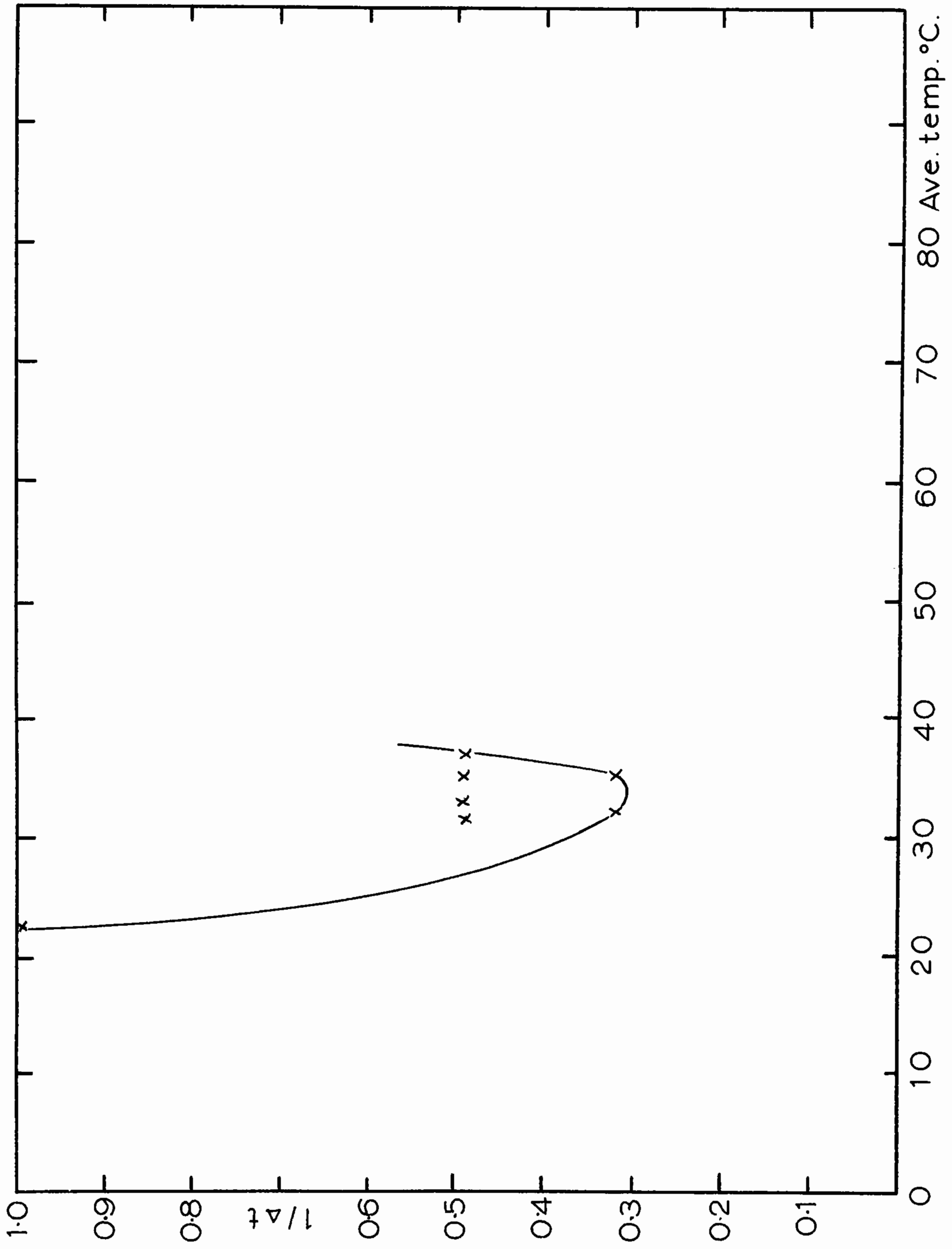


FIG. 51

Gold. Conditions for first appearance of dendrites.

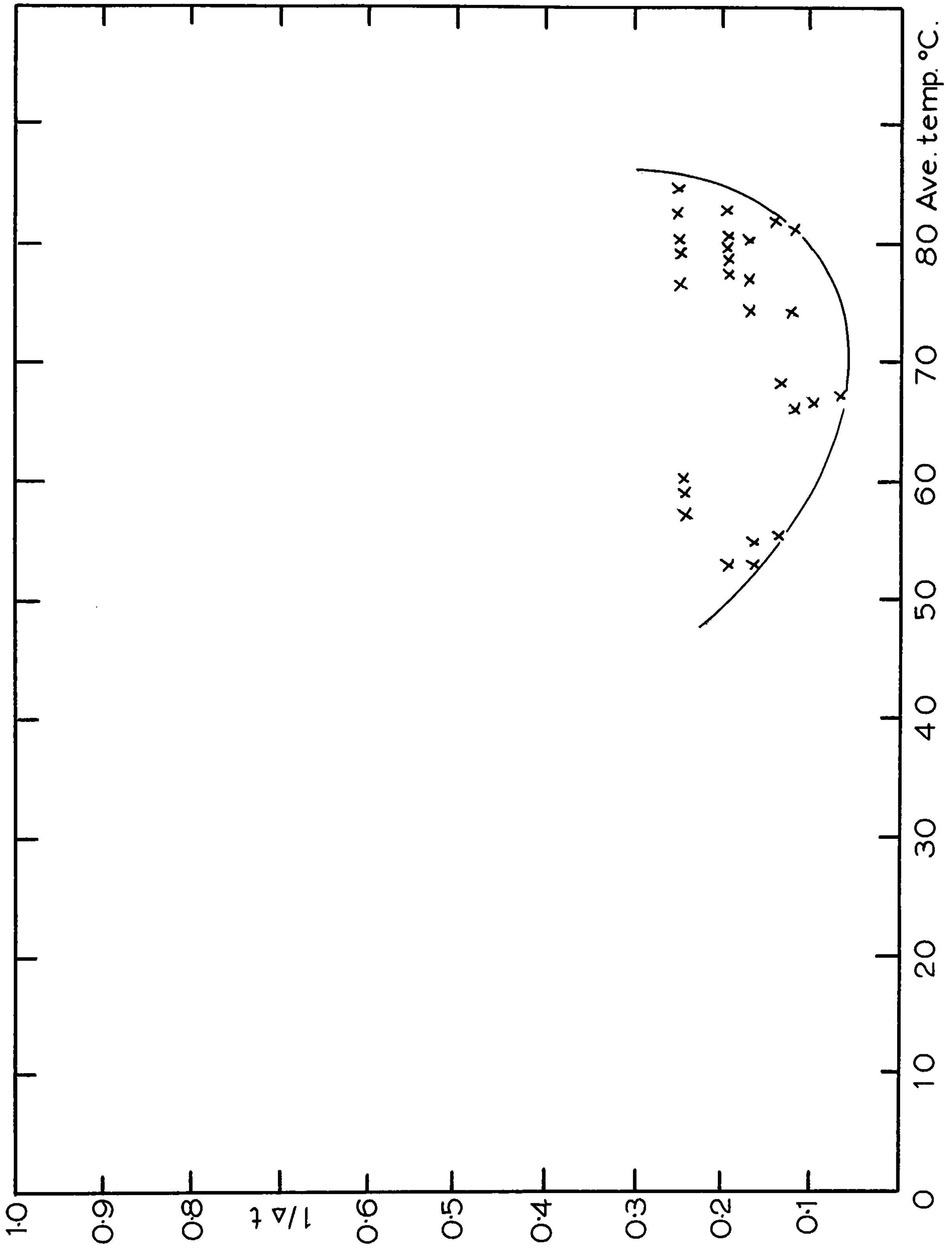


FIG. 52

Gold. Conditions for first appearance of hexagons.

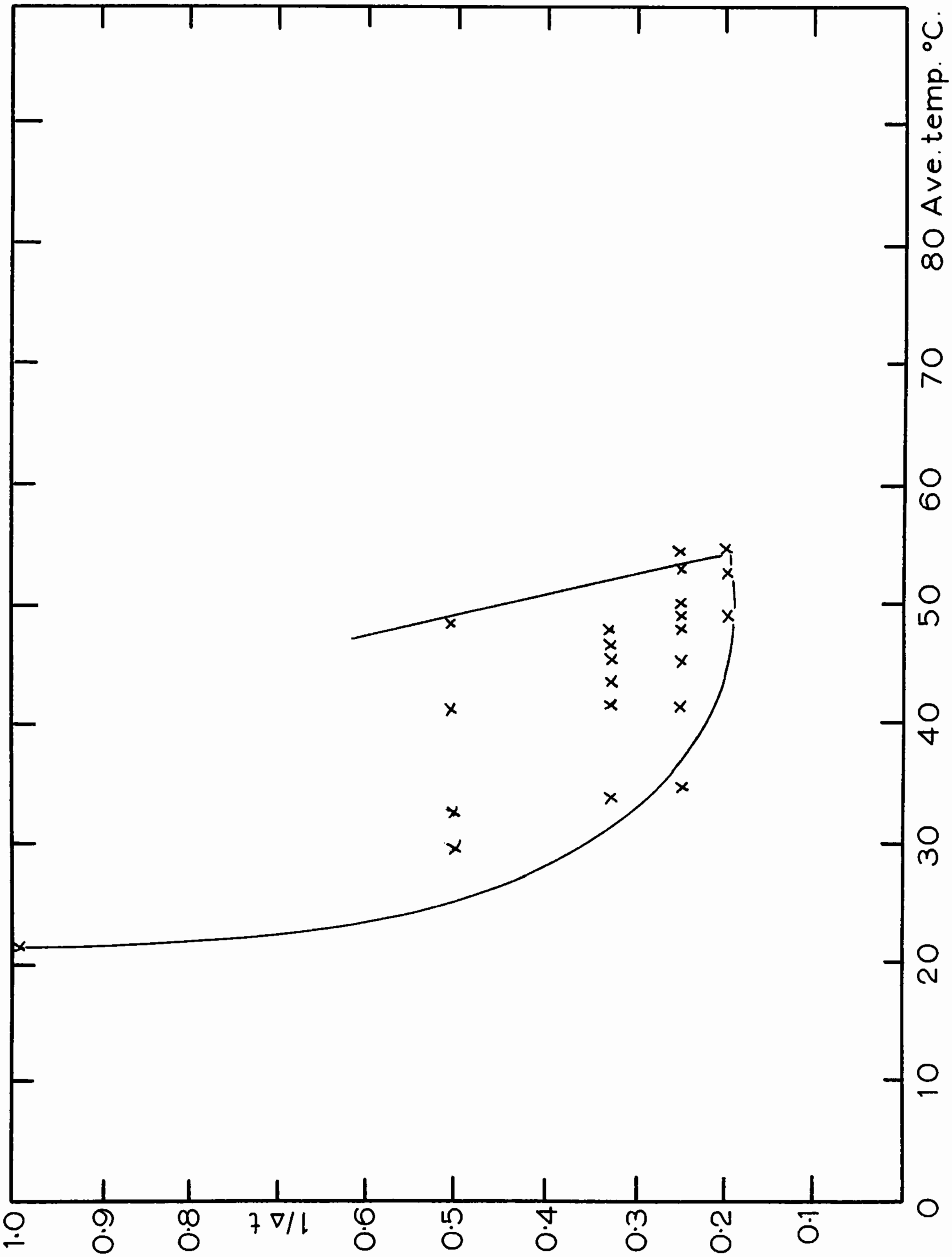


FIG. 53

Gold. Conditions for first appearance of rods.

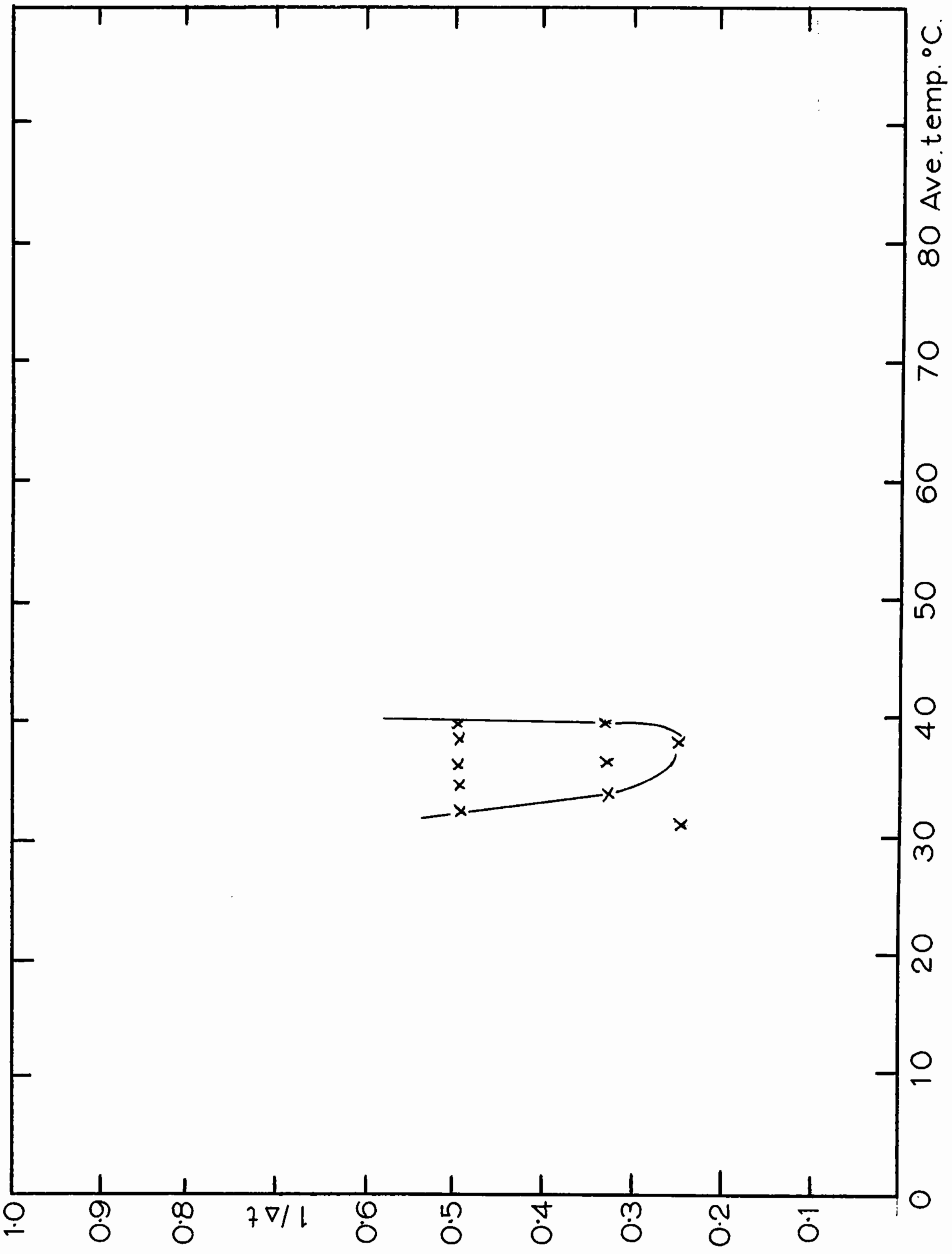


FIG. 54

Gold. Conditions for first appearance of squares.

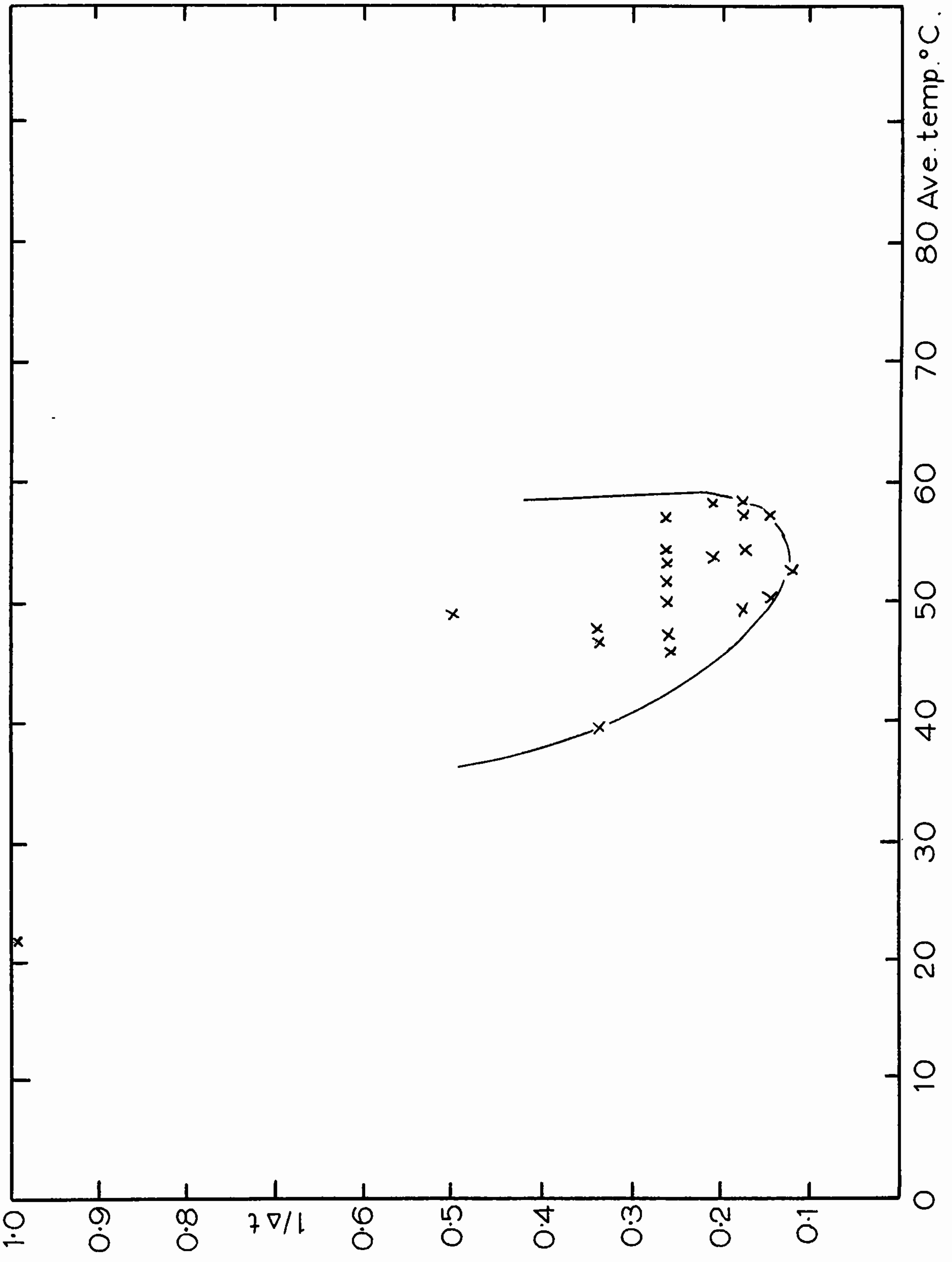


FIG. 55

Gold. Conditions for first appearance of trapezoids.

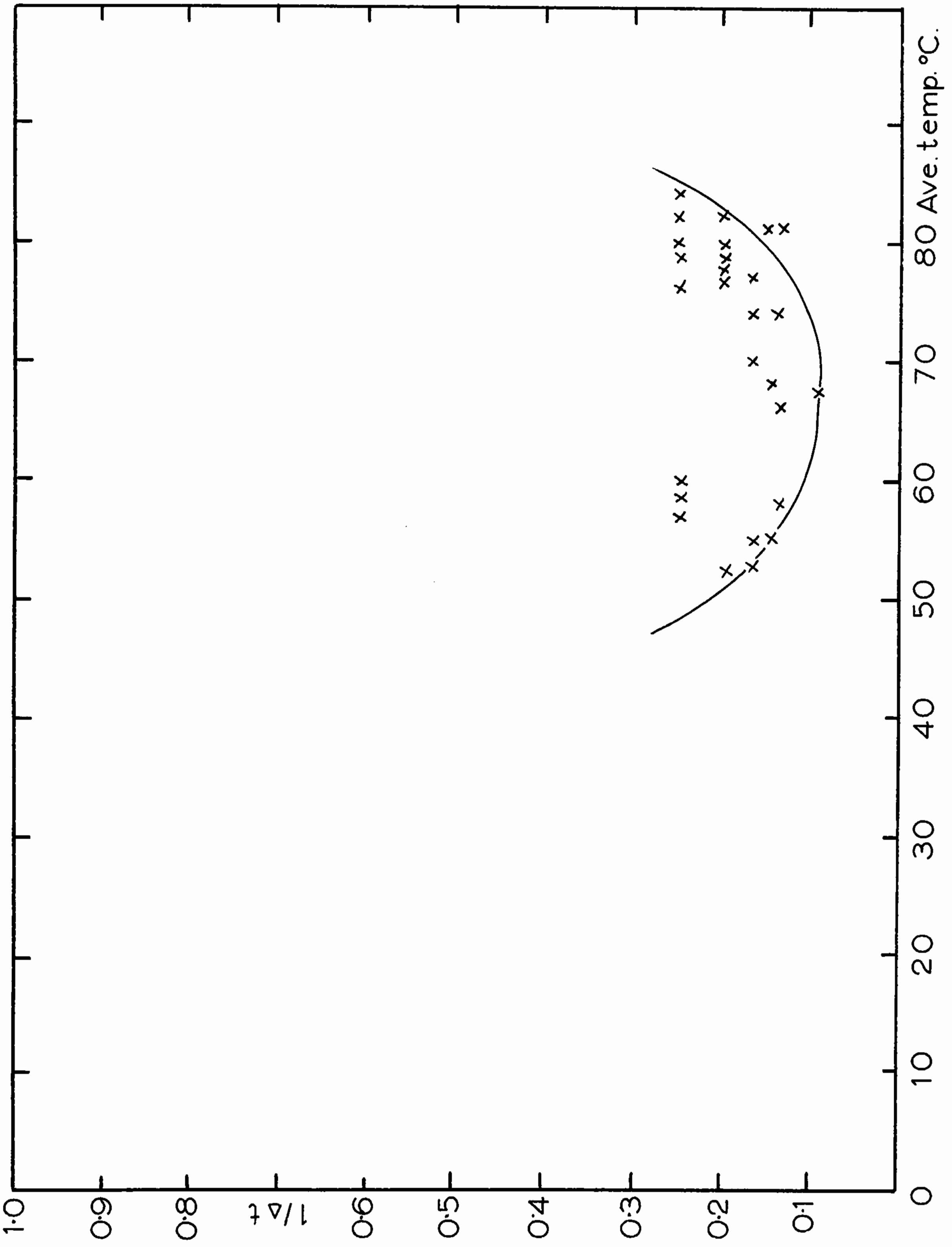


FIG. 56

Gold. Conditions for first appearance of triangles.

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