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FINAL REPORT

NUCLEATION AND GROWTH OF CRYSTALS UNDER CIRRUS  
AND POLAR STRATOSPHERIC CLOUD CONDITIONS

(NASA GRANT No. NAG-W-2572)

SUBMITTED TO

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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In a separate experiment, crystal growth was examined in a modified thermal vapor diffusion chamber over the range of cirrus temperature ( $-30$  to  $-70^{\circ}\text{C}$ ) and under controlled supersaturation and air pressure. The crystals grew at a velocity of  $1-2 \mu\text{m s}^{-1}$ , thickness  $60-70 \mu\text{m}$ , in the form of thin column crystals. Design criteria are given for a system to investigate particle growth down to  $-100^{\circ}\text{C}$ , (PSC temperatures) where nitric acid particles can be grown under similar control and in the form of hydrate crystals.

### **Publications and Presentations:**

- Teets, E. and J. Hallett, 1992: Nucleation and Crystallization of Highly Supercooled and Supersaturated Stratospheric Aerosol. 1992 AGU Fall Meeting, December 7-11, San Francisco, California.
- Hallett, J., 1994: Cirrus Ice Crystal Nucleation and Growth. AMS Eighth Conference on Atmospheric Radiation. January 23-28, 1994, Nashville, Tennessee. Conference Proceedings, 220-221.
- Hallett, J., J. G. Hudson, B. Queen and E. Teets, 1995: Aerosol and Cirrus Opacity. Paper No. AIAA 95-0544, 33rd Aerospace Sciences Meeting, Jan. 9-12, 1995, Reno, Nevada
- Hallett, J., Queen, B., E. Teets and J. Fahey, 1995: Nucleation Growth of Crystals under Cirrus and Polar Stratospheric Cloud Conditions. Technical Report - NASA Grant No. NAG-W-2572.
- Queen, B., E. Teets and J. Hallett, 1995: Supercooling and Glass Transition of Aqueous Solutions at High Concentration. To be published.
- Hallett, J., 1995: Crystal Growth from the Vapor at Cirrus and Polar Stratospheric Cloud Temperatures. In preparation.



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## TECHNICAL REPORT

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## ABSTRACT

Laboratory studies examine phase changes of hygroscopic substances which occur as aerosol in stratosphere and troposphere (sodium chloride, ammonium sulfate, ammonium bisulfate, nitric acid, sulfuric acid), under controlled conditions, in samples volume 1 to  $10^{-4}$  ml. Crystallization of salts from supersaturated solutions is examined by slowly evaporating a solution drop on a substrate, under controlled relative humidity, until self nucleation occurs; controlled nucleation of ice in a mm capillary U-tube gives a measured ice crystallization velocity at known supercooling. Two stages of crystallization occur for regions where hydrates exist. It is inferred that all of the materials readily exist as supersaturated/supercooled solutions; the degree of metastability appears to be slightly enhanced by inclusion of aircraft produced soot. The crystallization velocity is taken as a measure of viscosity. Results suggest an approach to a glass transition at high molality, supersaturation and/or supercooling within the range of atmospheric interest. It is hypothesized that surface reactions occur more readily on solidified particles - either crystalline or glass, whereas volume reactions are more important on droplets with sufficiently low viscosity and volume diffusivity. Implications are examined for optical properties of such particles in the atmosphere.

In a separate experiment, crystal growth was examined in a modified thermal vapor diffusion chamber over the range of cirrus temperature ( $-30$  to  $-70^{\circ}\text{C}$ ) and under controlled supersaturation and air pressure. The crystals grew at a velocity of  $1-2 \mu\text{m s}^{-1}$ , thickness  $60-70 \mu\text{m}$ , in the form of thin column crystals. Design criteria are given for a system to investigate particle growth down to  $-100^{\circ}\text{C}$ , (PSC temperatures) where nitric acid particles can be grown under similar control and in the form of hydrate crystals.

## I. Introduction

Change of phase in any physical system is critically linked to two processes. First, nucleation requires a thermodynamic driving force to overcome a potential barrier to form an embryo large enough to grow rather than dissipate under the ambient conditions. Second, the mass and heat transfer process is limited by both kinetic phenomena at the interface between the two phases and molecular transport processes towards and away from the interface in the bulk of the material. These considerations have general applicability for all phase changes - solid - liquid - vapor, whether as pure materials, as a gas mixture, or as a solution. A special case arises when mass transport can be neglected, as for example in crystallization from a pure melt or vapor where growth rate is entirely determined by kinetic and heat transport considerations. Even in this case, in practice, trace impurity segregation at the interface may eventually lead to some limitation resulting from mass transport considerations, as in the case of vapor - liquid - solid crystal growth. In a similar way, it is possible that heat transport can be neglected, and the situation be entirely controlled by mass or kinetic effects - as in the case of slow glass crystallization. In general, all three aspects of the crystallization process, heat transport, mass transport and interface kinetics must be assessed.

The nucleation process itself is often dominated by the presence of impurity nucleation centers, which prevent the occurrence of substantial supercooling or supersaturation. On occasion however, situations can be contrived where these centers are essentially absent and nucleation occurs by growth from large clusters of atoms and molecules arising by molecular fluctuations. This is homogeneous nucleation of the substance by itself as opposed to heterogeneous nucleation by impurity.

In practice, experimental techniques for the study of these phenomena conveniently follow from the simple process of taking smaller and smaller samples until the probability of having impurity induced heterogeneous nucleation is reduced to insignificant levels. Nature effects this technique very effectively in clouds in the atmosphere, which consist of water or solution droplets some 10  $\mu\text{m}$  diameter or below, many of which can supercool to temperatures near  $-40^\circ\text{C}$  (as pure water), or supersaturate to significantly lower temperatures to freeze by homogeneous nucleation. This situation is opposed to that of freezing of a bucket of water which readily occurs at less than a few degrees of supercooling by the chance occurrence somewhere in the

volume of one impurity nucleus. Similar considerations apply for the solidification of all substances. Such phenomena have been suggested as being important in the small water droplets which readily occur in lenticular clouds at temperatures near  $-40^{\circ}\text{C}$  (Heymsfield and Milosovich, 1993) and also at nuclei lower temperatures for solutions of sulfuric and nitric acid in higher level clouds - Polar Stratospheric clouds and higher noctilucent clouds at temperatures down to below  $-50^{\circ}\text{C}$  (Hallett 1965).

This investigation is concerned with understanding phase changes related to solutions which may comprise such high level clouds, and subsequent crystal growth, in particular it is concerned with techniques for investigating specific classes of metastability and phase change which may be important not only in Polar Stratospheric Clouds but in all atmospheric aerosol in general. While the lower level atmospheric aerosol consists of mixtures of  $(\text{NH}_4)_2(\text{SO}_4)$ ,  $(\text{NH}_4)$ ,  $\text{HSO}_4$ ,  $\text{NaCl}$  among others, aerosol at PSC levels is composed of acid aerosol, either injected from volcanic events (such as Pinatubo) or having diffused upward from the lower atmosphere. In particular, sulfuric acid and nitric acid are known to occur at Polar Stratospheric Cloud levels, and are suspected of catalyzing ozone destruction reactions by adsorption on surfaces of crystallized particles (for example. Molina et al, 1993). Such particles may result from water absorption by the acid aerosol, followed by crystallization as hydrates or ice depending on temperature and composition.

A major question arises as to the extent to which such particles supercool (supersaturate) prior to crystallization, the nature of the crystallization process itself in these droplets, and the nature of subsequent growth from the vapor of crystals in the form of ice or hydrate depending on the environmental conditions - temperature or vapor pressure of water vapor (relative humidity) and acid. A crucial first question is the occurrence of solutions which supersaturate. It is well known (see Pruppacher and Klett, 1980) that aerosol particles in the lower atmosphere, of composition listed above, supersaturate substantially and contribute to a hysteresis in visibility. The amount and time dependence of such metastability is ill understood, as is the dependence on insoluble aerosol (particularly soot) to nucleate such Metastable particles. Identical questions occur for stratospheric clouds. The present study has centered on three approaches:

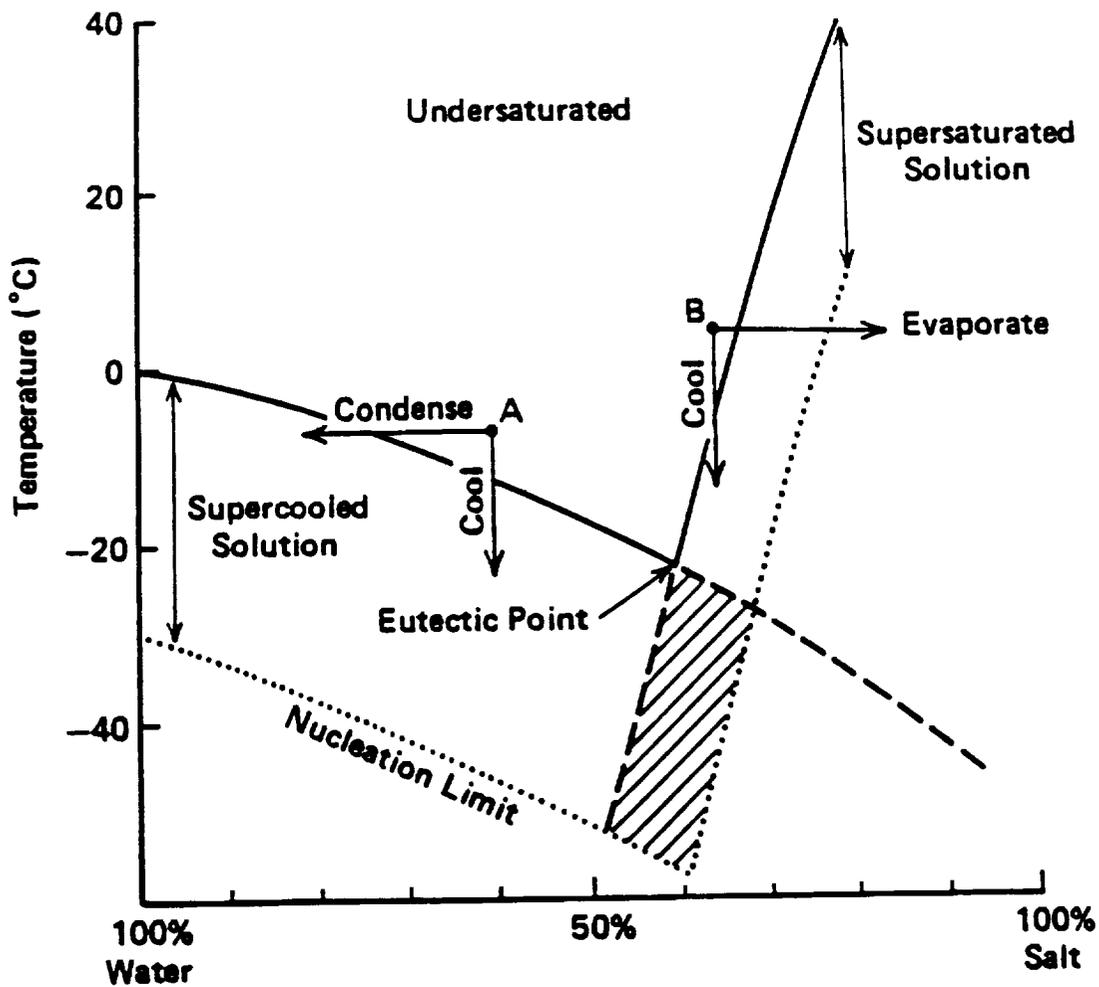
- 1) The extent of supercooling (with respect to ice) and supersaturation (with respect to hydrate or solute).
- 2) The nature of crystal growth in acid solutions of specific molality.
- 3) Development of techniques for the growth from the vapor of crystals at low temperatures substrate and on a pre-existing aerosol and controlled supersaturation.

The rationale for this study comes from a consideration of an isolated particle serving as a substrate for further growth from the vapor and as a substrate for adsorption/absorption of trace chemical species and heterogeneous catalysis. Thus the phase of the particle is of importance. Several possibilities exist. Existing solution aerosol droplets grow by cooling, absorbing water vapor and soluble gases to give a droplet of composition determined by the Köhler relation. Such particles may supercool with respect to ice and/or supersaturate with respect to solute and hydrate phases (Fig. 1). Further, for high concentrations of solute, the solution viscosity increases to give a glass at sufficiently low temperatures, thus inhibits internal diffusion of adsorbed trace components.

Surface concentrations and reaction rates are likely to be larger than volume reactions, and more liable to photochemistry in the short UV which is absorbed over very short distances, Ohtake (1993) has demonstrated that indeed sulfuric acid solutions substantially supersaturate; Fox et al (1995) demonstrate the occurrence of metastable phases in the presence of sulfuric acid, nitric acid mixtures; Wooldridge et al (1995) discuss details of phase equilibrium.

## **2. Experimental Approach**

The introduction raises specific questions concerning the phase and physical properties of particles which could be present in high level cirrus and stratospheric clouds at low temperatures. Experiments are designed to investigate specific aspects of these properties, bearing in mind that the smaller the particle the more likely it is to be in a metastable state because of reduced nucleation probability.

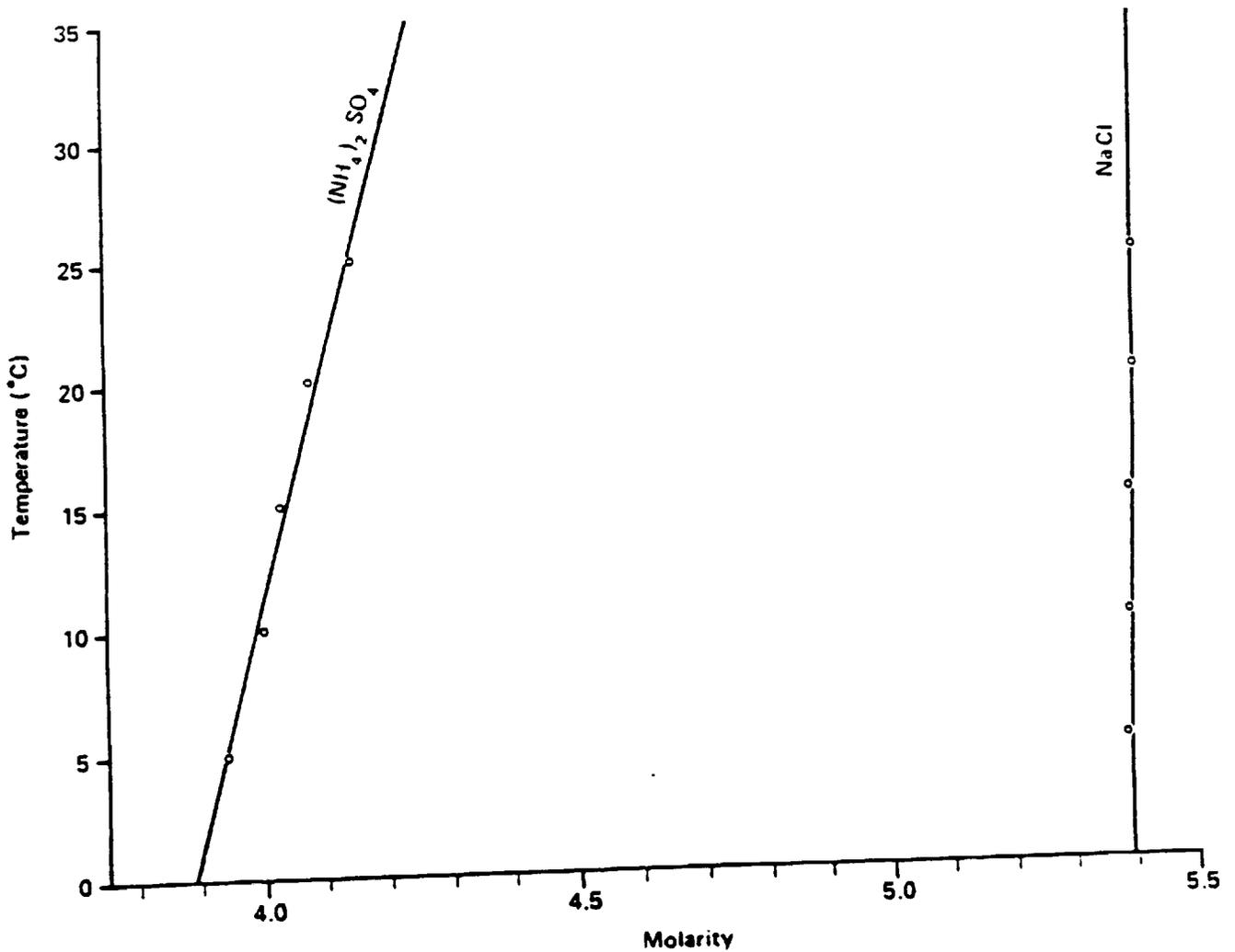


**Fig. 1:** Schematic of possible instabilities in a solution which forms eutectic (for example NaCl). The full lines are equilibrium concentrations with respect to ice and crystal; the dotted lines represent the approach to homogeneous nucleation for finely divided samples. From undersaturated conditions, supercooling can be achieved by condensation or cooling (Point A); supersaturation can be obtained by cooling or evaporating (point B).

The first class of experiments was designed to supercool/supersaturate solutions under controlled conditions and examine the in-situ growth of crystals from bulk solutions. For supercooling of a few degrees, this is readily accomplished by cooling a volume of about 1 ml in a small cell below its equilibrium crystallization point and nucleating by inserting an ice single crystal (Hallett, 1964; Harrison et al, 1987). In order to achieve large supercooling, it is necessary to use smaller volumes; in this case it is convenient to contain the sample in a glass U-tube immersed in a cold bath, with ends emerging vertically through the liquid interface to higher outside temperature. Nucleation is achieved by inserting a LN<sub>2</sub> cooled wire. This technique was used by Yang and Good (1966) and Yeh, et al (1987) to investigate growth of ice in supercooled water and antifreeze glycoprotein solutions. It gives some uncertainty at small Supercooling as the ice growth is faster along the walls than in the bulk of the solution, but is less ambiguous at larger supercoolings (> few °C) where the wall enhancement effect is no longer important. The crystallization velocity, gives a measure of the viscosity, which drops to low values as the solution becomes a glass. This can be formally expressed as a crystallization velocity:

$$V = A \exp -\frac{B}{kT} \Delta T^c$$

where A, B, and c are constants, with c about 2, T is temperature and ΔT the supercooling. Whilst it is easy to achieve supercooling by simply cooling a solution, it is more difficult to obtain supersaturation by cooling (Fig. 1). Saturation concentration is not often strongly temperature dependent (Fig. 2), so cooling saturated measurements is not a good technique. Furthermore, it turned out that for the substances investigated (ammonium sulfate, ammonium bisulfate) that it was difficult to prevent self nucleation in contact with a glass cell. This led to development of a second technique, where a drop of solution on a polyethylene substrate was exposed to an atmosphere at controlled relative humidity and slowly evaporated, thus increasing the concentration at constant temperature. Although controlled nucleation was a possible technique in this case, it was found in practice that the largest supersaturations were best obtained from continuous video of the drop until self nucleation occurred - there was sufficient spread of events to give adequate measurements over the attainable range of supersaturation.



**Fig. 2:** Temperature dependence of saturation concentration of ammonium sulfate and sodium chloride.

Results obtained from this class of study, although not reaching the glass state, specifically show that growth rate of the crystals is no longer increasing with the thermodynamical driving force (supercooling or supersaturation). Furthermore, this study shows that crystallization can occur in two phases, first ice and second hydrate, the hydrate being subject to the same considerations of nucleation and growth as the ice in the first phase of nucleation. Thus growth occurs in a higher concentration of solution because of removal of solvent into ice during the final stage of crystallization.

The second class of experiment investigated the technology of a chamber to grow crystals from the vapor, at low temperature, and under controlled supersaturation and air pressure. Previous experiments had covered the range of temperature important for crystal growth in the troposphere down to about  $-30^{\circ}\text{C}$  (Alena et al, 1990; Hallett, 1987). The new chamber design extends the range to lower temperature to cover cirrus crystal growth. Ideally this would cover the range  $-80$  to  $-100^{\circ}\text{C}$ , lowest temperatures at which stratospheric clouds form. The first approach was to use a static thermal diffusion chamber, with thermoelectric cooling modules to achieve independent control of top and bottom plates. This approach was limited by viscosity of fluid cooling the thermoelectric elements, and in practice the lowest temperature reached has about  $-80^{\circ}\text{C}$ .

The principle of operation of the diffusion chamber is transport of heat and vapor between two ice coated plates maintained at constant temperature. In the absence of convection, as is the case for horizontal plates with the bottom colder than the top, there is a near linear gradient of temperature and vapor density (or pressure) between top and bottom plates. The saturation vapor density falls off approximately exponentially with temperature and, assuming saturation at each plate as given by the Clausius-Clapyeron equation, the ice supersaturation can be computed and has a maximum difference somewhat below the center of the chamber, with a magnitude which increases with temperature difference. Crystal growth can take place on a vertical fiber, and the crystal habit and growth rate observed by video recorded microscopy from outside the chamber.

### 3. Crystallization and Freezing of Solutions

Solution droplets in the atmosphere originate by dissolution of hygroscopic nuclei as the relative humidity increases, to form haze droplets and ultimately cloud droplets. At temperatures below  $0^{\circ}\text{C}$ , there occurs the standard freezing point depression, which is given by

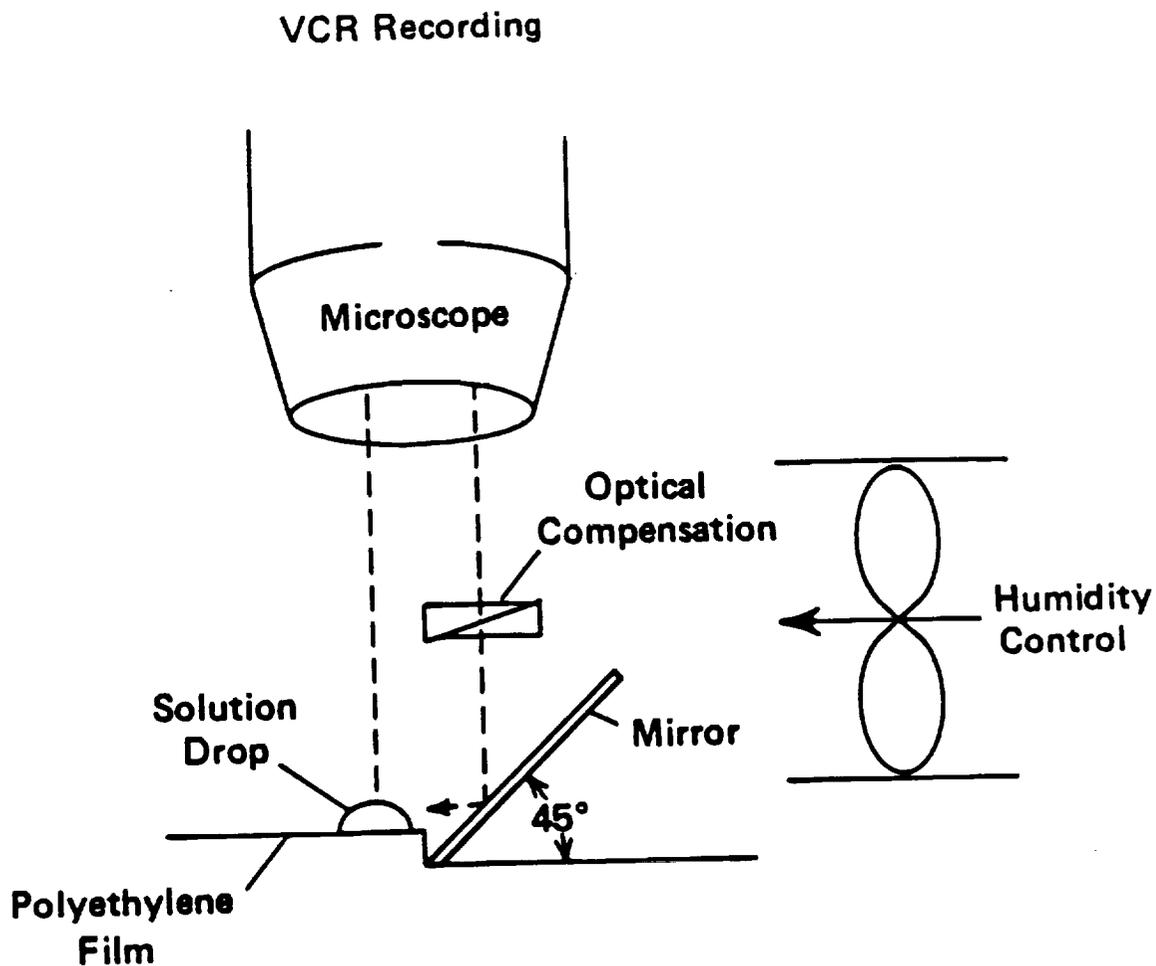
$$\Delta T = i m \times 1.86^{\circ}\text{C} \dots\dots\dots (1)$$

where  $i$  = van't Hoff factor,  $m$  = molality.

A further supercooling can take place below this equilibrium, which for particle free solution and a drop smaller than a few  $\mu\text{m}$  approaches  $40^\circ\text{K}$ . It is assumed with some justification, (see Pruppacher and Klett, 1980) that these two terms are additive. As droplets grow and dilute, so the equilibrium freezing point depression lessens, and the freezing probability, at a particular temperature increases, approaching  $-40^\circ\text{C}$  for dilution beyond  $m/10$ . In the case of both ice crystallizable solute and hydrates, a hysteresis occurs such that the droplet is liquid beyond its equilibrium point as it supercools or supersaturates; nucleation eventually occurs either of ice, hydrates, solute or a combination of these, possibly as a eutectic at sufficiently low temperature. As the drop temperature is raised differing components melt at different temperatures. Experiments are described for important components of the atmospheric aerosol in the troposphere and stratosphere, particularly ammonium sulfate, ammonium bisulfate, sodium chloride, nitric acid, sulfuric acid.

### **3a. Nucleation and Crystal Growth of Solute Crystals in Highly Supersaturated Solutions**

A technique was designed for investigation of phase change at temperatures above  $0^\circ\text{C}$ , so that ice formation was not involved. Cooling of bulk liquid and capillary tubes of solutions to significant supersaturation was tried unsuccessfully, as nucleation at the glass - solution interface prevented significant supersaturation. The technique found to work was to place a dry crystal of known weight ( in the neighborhood of  $20\ \mu\text{g}$ , size about  $250\ \mu\text{m}$ ) on a hydrophobic surface (polyethylene on a glass slide) and expose the crystal to high humidity by slow circulation of moist air from an outside chamber. The crystal behavior was continually viewed by VCR. The microscope used an optical technique whereby the drop was viewed from top and side simultaneously (Fig. 3). This enables the volume of a drop to be estimated; the molality is computed from known dry crystal mass. The experiment consists of completely dissolving the crystal in high relative humidity then gradually reducing the air humidity by controlling mixture of dry/moist air so that the drop slowly evaporates. The rate process is important, and needs to be sufficiently slow to prevent significant gradients of concentration within the drop. Taking  $r = 100\ \mu\text{m}$ ,  $D$ , coefficient of solute diffusivity as  $10^{-4}\ \text{cm}^2\ \text{s}^{-1}$  the time constant for equilibrium  $\sim r^2/D$  is about 1 second. Hence evaporation over periods of  $> 100\ \text{s}$  should



**Fig. 3:** Technique for measurement of solute crystallization velocity. A solution droplet is grown by exposure of a known mass crystal to high relative humidity; supersaturation is produced by slow evaporation at lower relative humidity. The optical system enables the height and radius of droplets to be continuously recorded.

prevent formation of significant gradients between drop surface and center; in practice the drop was equilibrated for about 1000 seconds. Nucleation occurred at a specific site, followed by growth of crystals through out the drop. The linear velocity of growth of crystals is readily measured from the video record (Fig. 4). This shows that the velocity does not change across the droplet, confirming the absence of a significant interval gradient of supersaturation. Dependence of crystallization velocity (at constant temperature +20°C) on supersaturation is obtained by combining results of many experiments. As described earlier, it was not practical in this technique to achieve controlled nucleation. Larger supersaturation was achieved by use of a fresh substrate and removal of environmental aerosol in the humidity chamber.

The results are shown in Figs. 5, 6 for ammonium sulfate and ammonium bisulfate. Since some of the growth velocities measured may not be in the plane of the microscope, the velocity is reduced by the cosine of the angle. The angle is not readily determined. The data assembled in these two figures is therefore analyzed by taking the envelope of maximum crystallization velocities, bearing in mind this measurement uncertainty. This shows in each case that the crystallization velocity increases to a maximum and then decreases as the supersaturation increases. This is indicative of increasing viscosity of the solution, and suggests that a glass transition may occur as velocity extrapolates to zero. In the atmosphere, haze particles have a volume some  $10^6$  less than is required for the visualization of the crystallization phenomena, as in these experiments. It would be anticipated that much larger supersaturation could prevail to permit the glass transition to be reached.

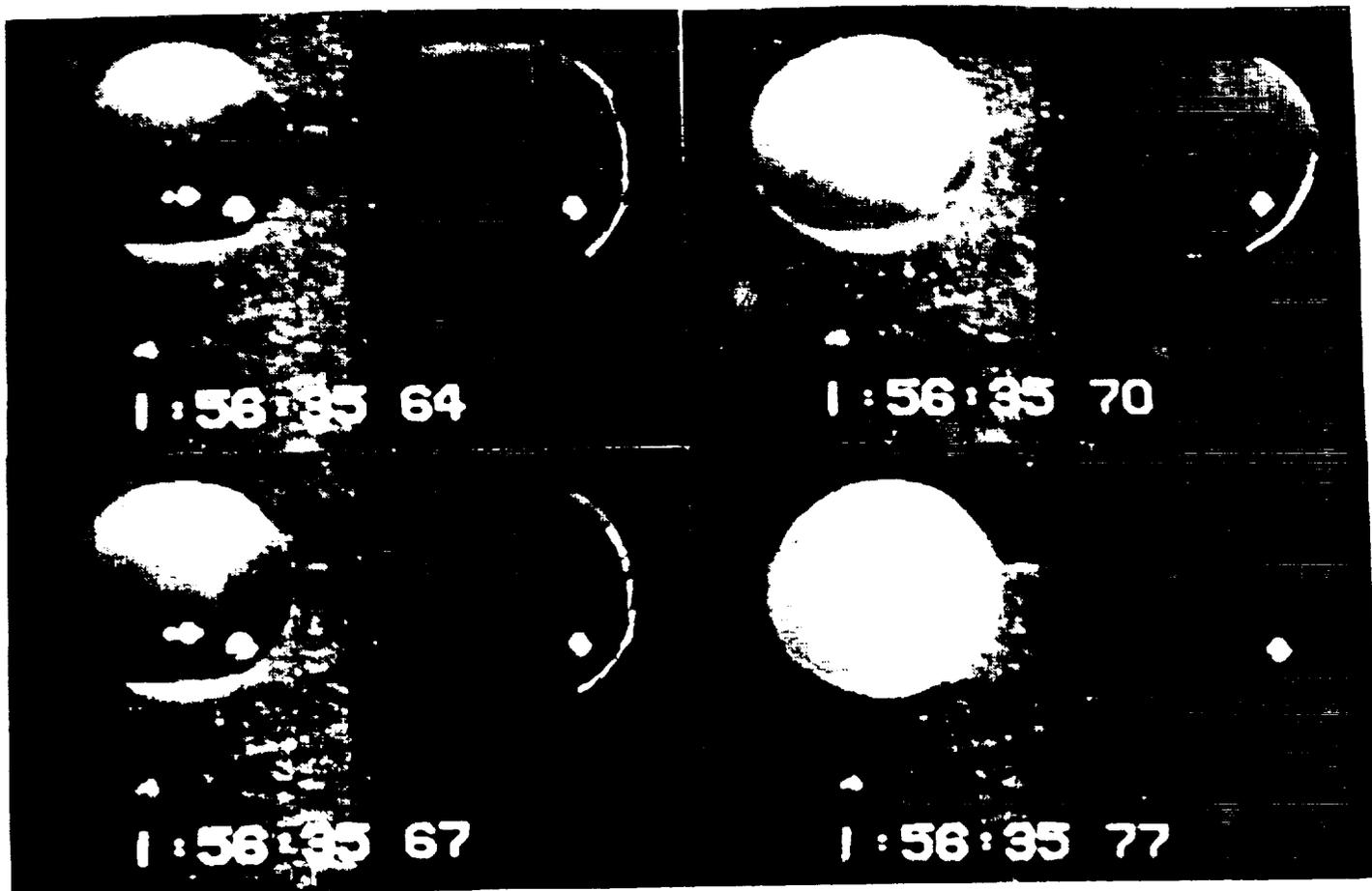
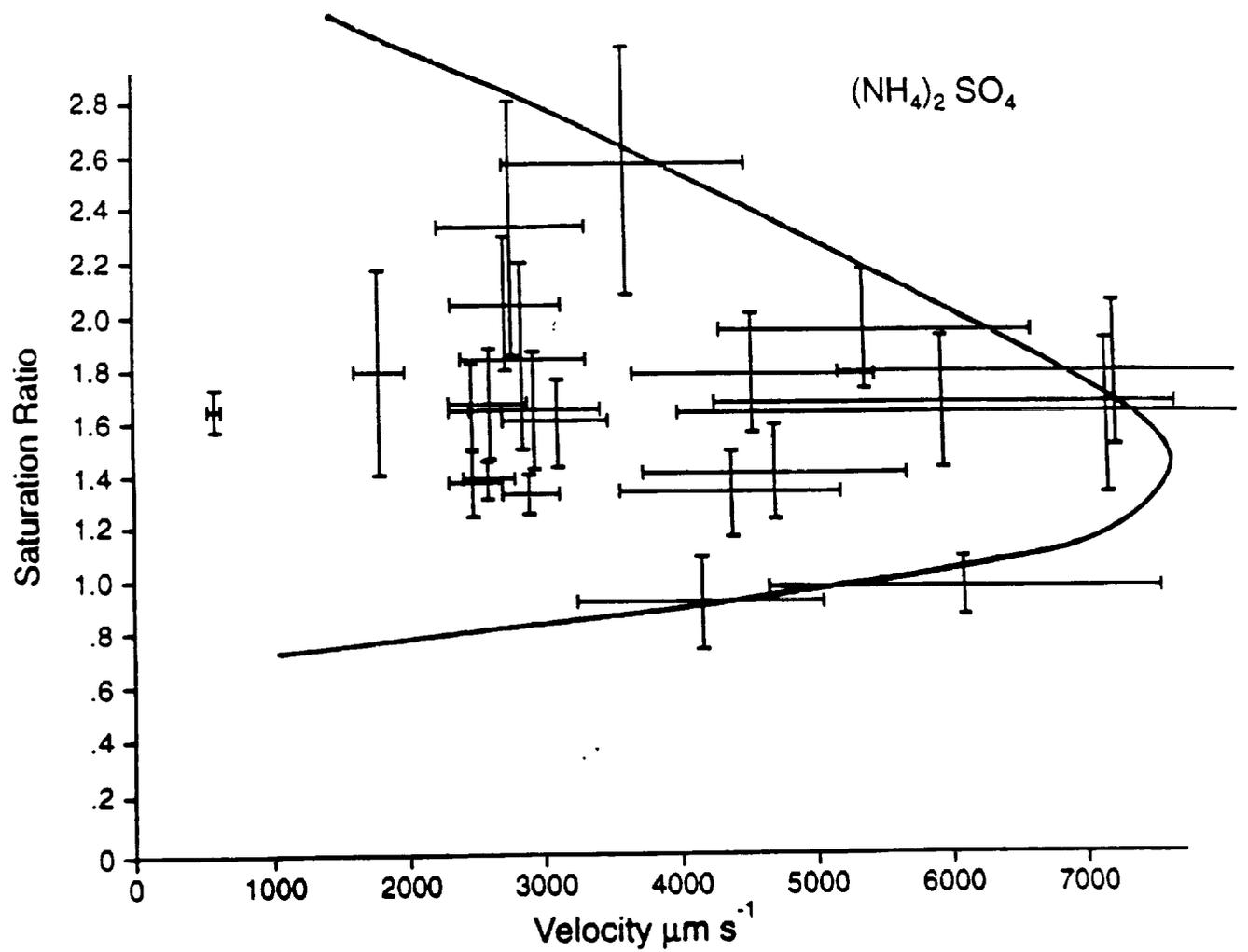
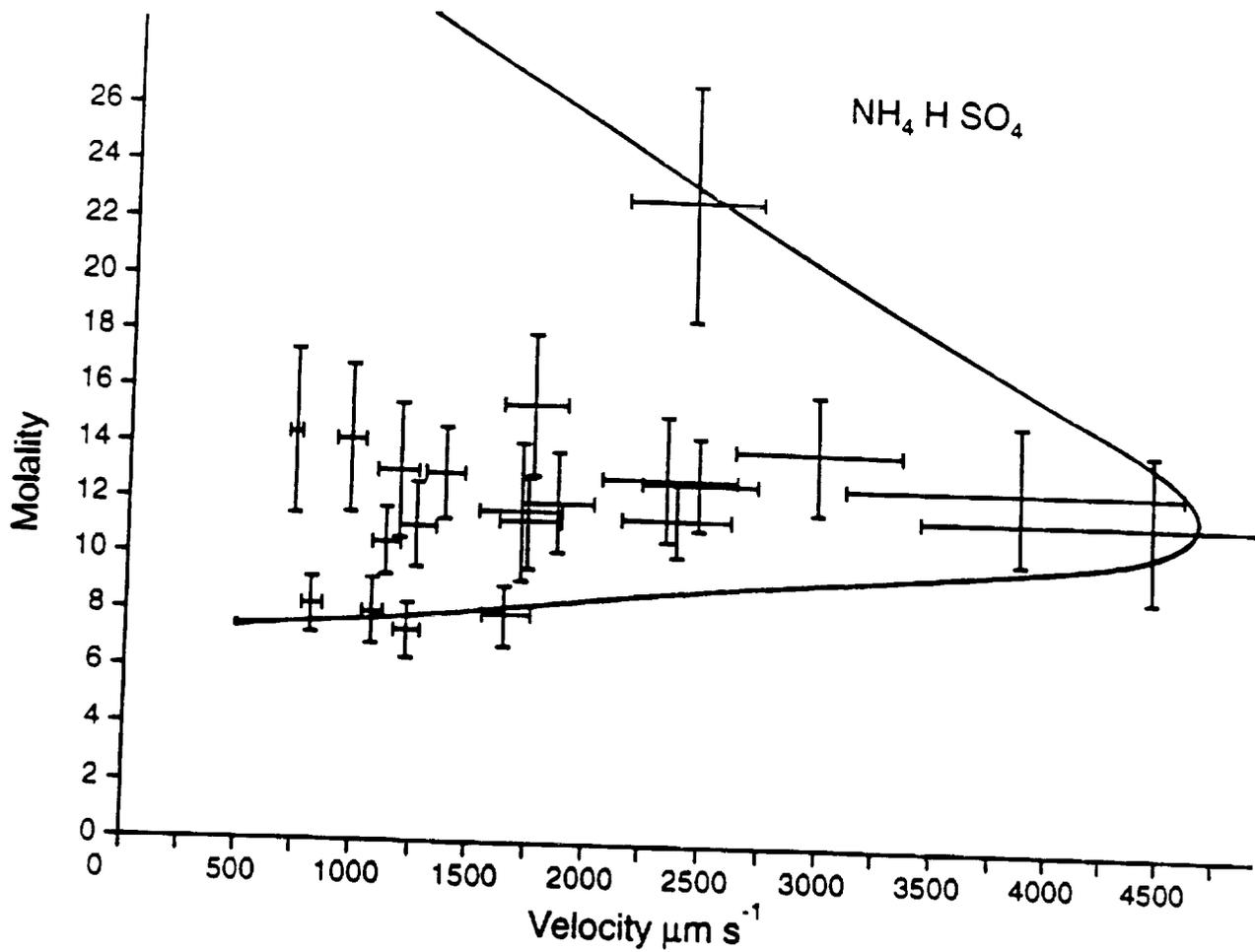


Fig. 4: Stages in crystallization of an ammonium sulfate drop (times to 0.01 seconds). The side view of the drop is to the right in each case.



**Fig. 5:** Summary of data from all experiments for ammonium sulfate solution. Temperature  $+22^\circ\text{C}$ . Error bars relate to uncontrolled crystallization direction. The full line is the envelope of maximum velocity at different supersaturations.



**Fig. 6:** As figure 5 for ammonium bisulfate. The plot is against molality as equilibrium saturation data is not available.

### 3b. Nucleation and Growth of Ice in Supercooled Solutions

Initial studies utilized the techniques of earlier work cited above, with controlled nucleation by a single ice crystal. This technique failed to achieve supercooling much below 5° C for values ~ 1 ml, so the capillary tube technique was adopted. The crystallization velocities at small (< 5° K) supercooling are somewhat erratic in this technique for a reason similar to the velocities of crystal growth in the previous section: the crystals grow at an angle to the tube direction, which give a lower value (Fig. 7). Alternatively dendrites grow along the surface of the tube which give a higher value of velocity. At larger supercooling, > 5° K these effects were no longer significant and as viewed from above, the growth interface advanced uniformly across the width of the tube, with a structure of fine dendrites, whose dimension decreased with increase of supercooling.

The dimension of the capillary tube was a compromise between practical concerns as inserting a nucleating crystal or a LN<sub>2</sub> cooled wire for nucleation, and minimizing the volume of liquid supercooled to achieve larger supercooling. A diameter of about 2 mm was used. The capillary U-tube was immersed in a constant temperature circulating bath of heat transfer fluid which enabled uniformity and control to ± 0.2° C. The velocity was measured as the transit time between two points 5 cm apart on the capillary, recorded visually or by VCR depending on the magnitude of the velocity.

The results are displayed as plots of crystallization velocity against supercooling below the equilibrium melting point of the solutions. This was determined by raising the temperature of the bath until complete melting just occurred. It is noted that although the freezing point depression can be computed, in principle, from equation (1), 'i' for highly concentrated solutions is certainly less than the ideal value for dilute solutions (the number of ions). There is little information on this, but it may be as low as 0.5 x # of ions (Chan et al, 1992).

# Growth Velocity for Tube Diameter

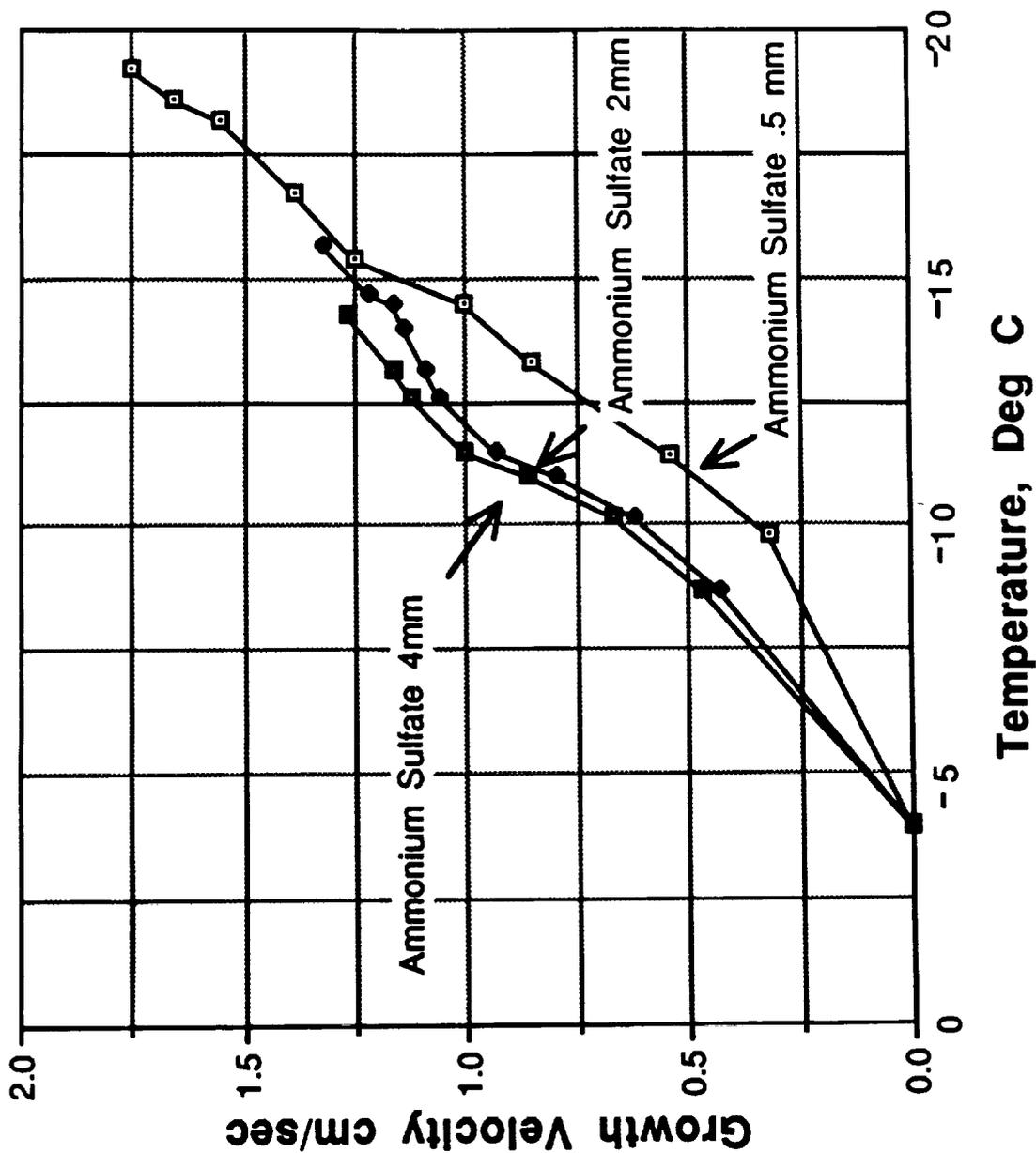
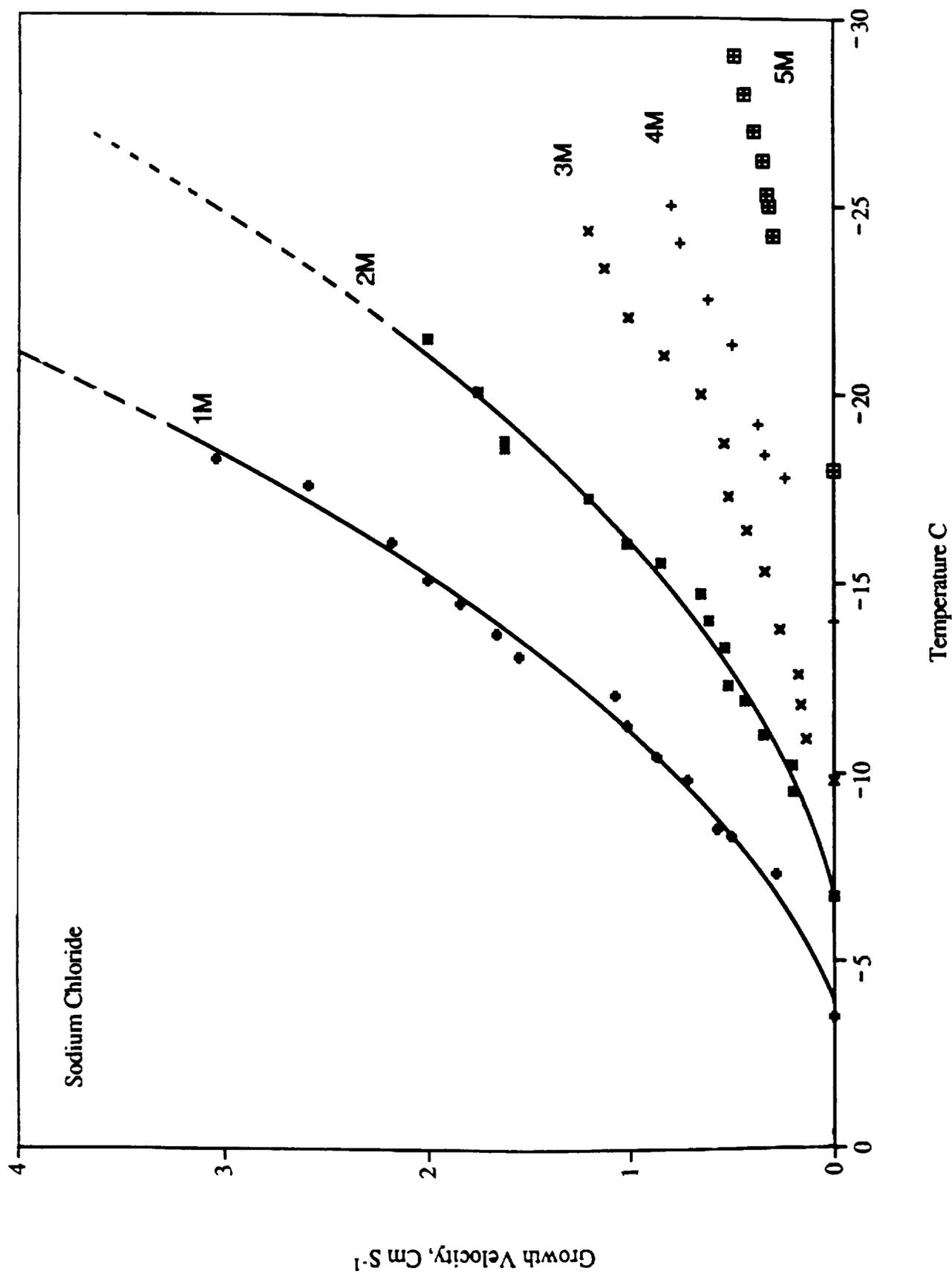


Fig. 7: Crystallization velocities for crystal growth in glass tubes of differing diameter at different supercooling.

Each graph represents crystallization velocities for a set of molalities. It is clear that at small supercooling and molality the crystallization velocities increases with supercooling. This is consistent with earlier results, as is the decrease with molality for a given supercooling (Ohara and Reid, 1973). As supercooling increases, it is clear that the increase slows and approaches a maximum. This is indicative of the increasing solution viscosity. It suggests an approaching glass transition, as found in the first experiment but at substantially lower temperatures than could be obtained using these techniques. A system needs to be designed for measurement of growth rates at larger supercooling to fully confirm this effect. Figs. 8, 9 and 10 show measurements of linear crystallization velocity for the indicated molalities; with the furthest point to the right representing the maximum supercooling which could be achieved. In each case, there is a change in the form of the curve with concentration somewhere between 1 m and 2-3 m, where data suggest a levelling off of the increase of growth velocity with supercooling. Fig. 11, 12 and 13, show similar cases for nitric acid and sulfuric acid. Figures 14 and 15 show the results for nitric acid - sulfuric acid mixtures showing an increased velocity for a mixture compared with pure solutions of either. A summary of achieved supercoolings is shown on Fig. 16, 17. Also shown are the equilibrium melting points from earlier data, and from the present observations (compare triangles and solid cells). The equilibrium point is notoriously difficult to measure under these conditions, in particular because of visibility problems of the crystals near the equilibrium point. The observations are therefore to be presented with caution as probably are the earlier results.

A limited number of runs were carried out with soot scraped from the Blackbird aircraft exhaust. About 0.2g soot was dispersed in 15 ml of the mixed acids. By far the most important effect is a decrease of the freezing rate, lowering the enhanced rate of the mixture to about its original value Fig. 18. The results also showed a slight increase in the maximum supercooling attainable for 3M solutions of about 5°K.

A phenomena was observed for sulfuric acid which clearly demonstrated the presence of a hydrate. This consisted of a sequential crystallization. Initial crystal growth occurred in the normal way. A second crystallization separately occurred, at a velocity of about 0.1 of the first wave which appeared whiter, suggesting the presence of very fine crystals. This occurred only at larger supercoolings, and could not be reliably reproduced.



**Fig. 8:** Crystallization velocity of ice in sodium chloride solution. Each point represents one experiment at the given supercooling. The point at zero growth velocity represents equilibrium conditions.

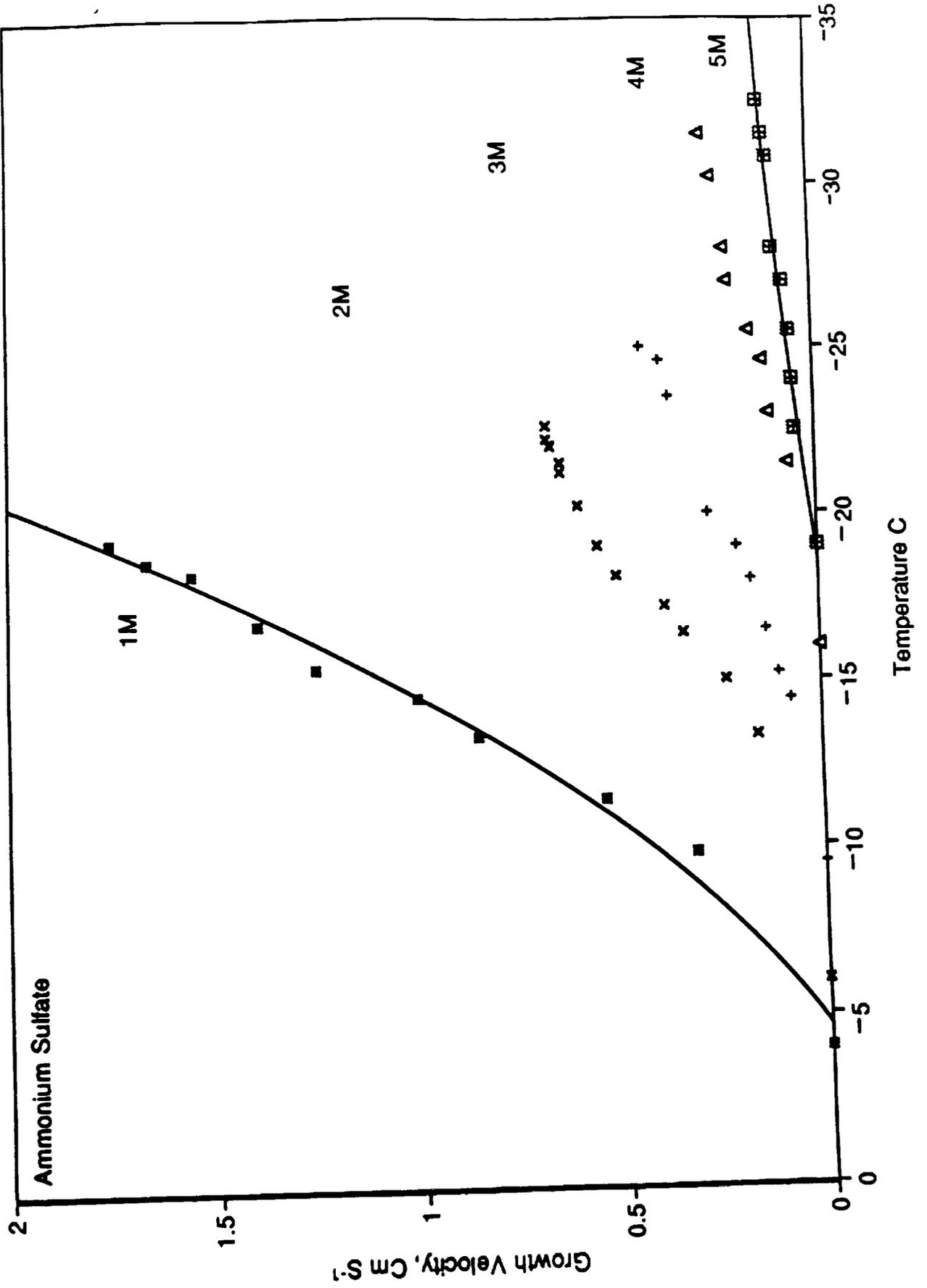


Fig. 9: As figure 8, for ammonium sulfate solution.

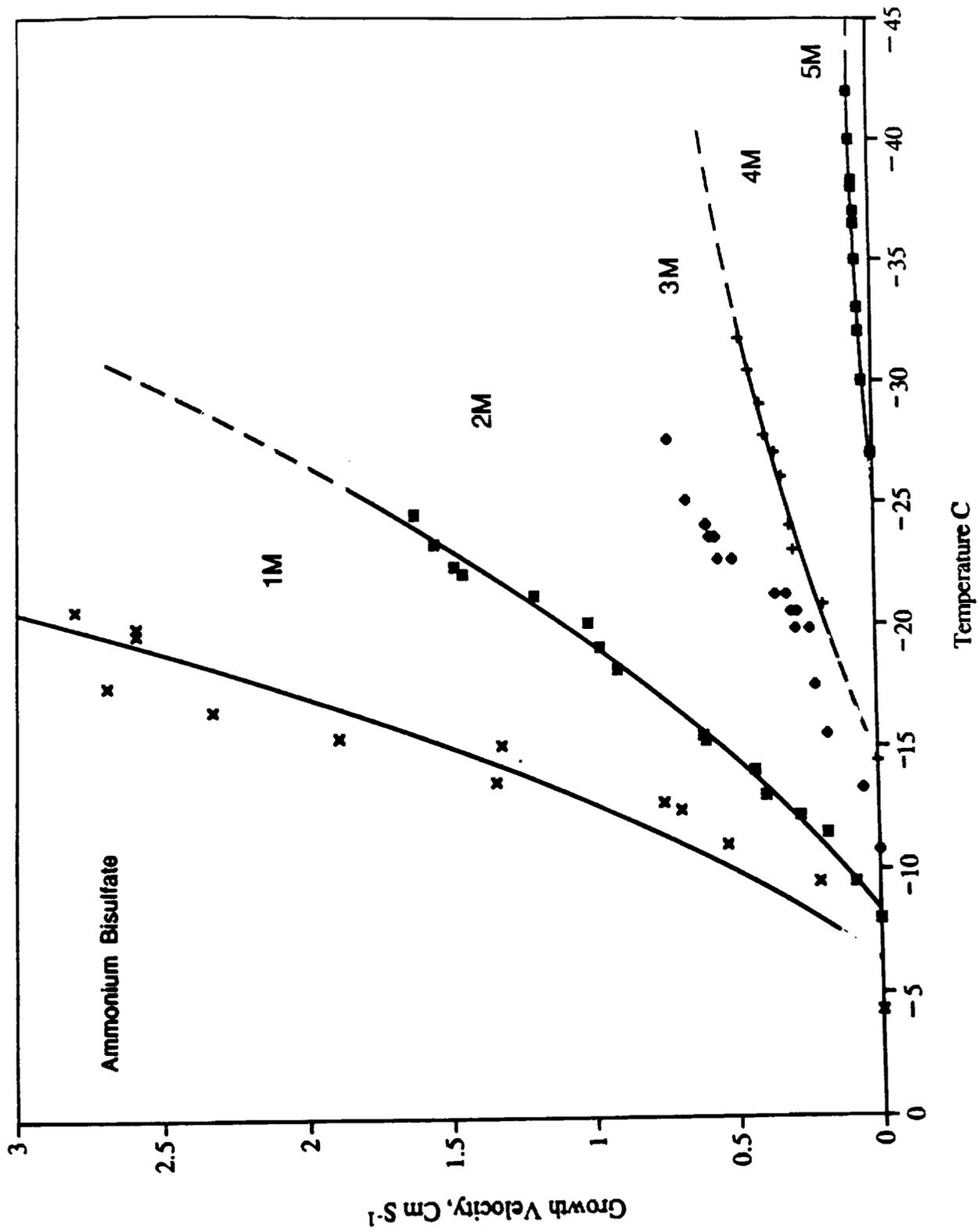


Fig. 10: As figure 8, for ammonium bisulfate solution.

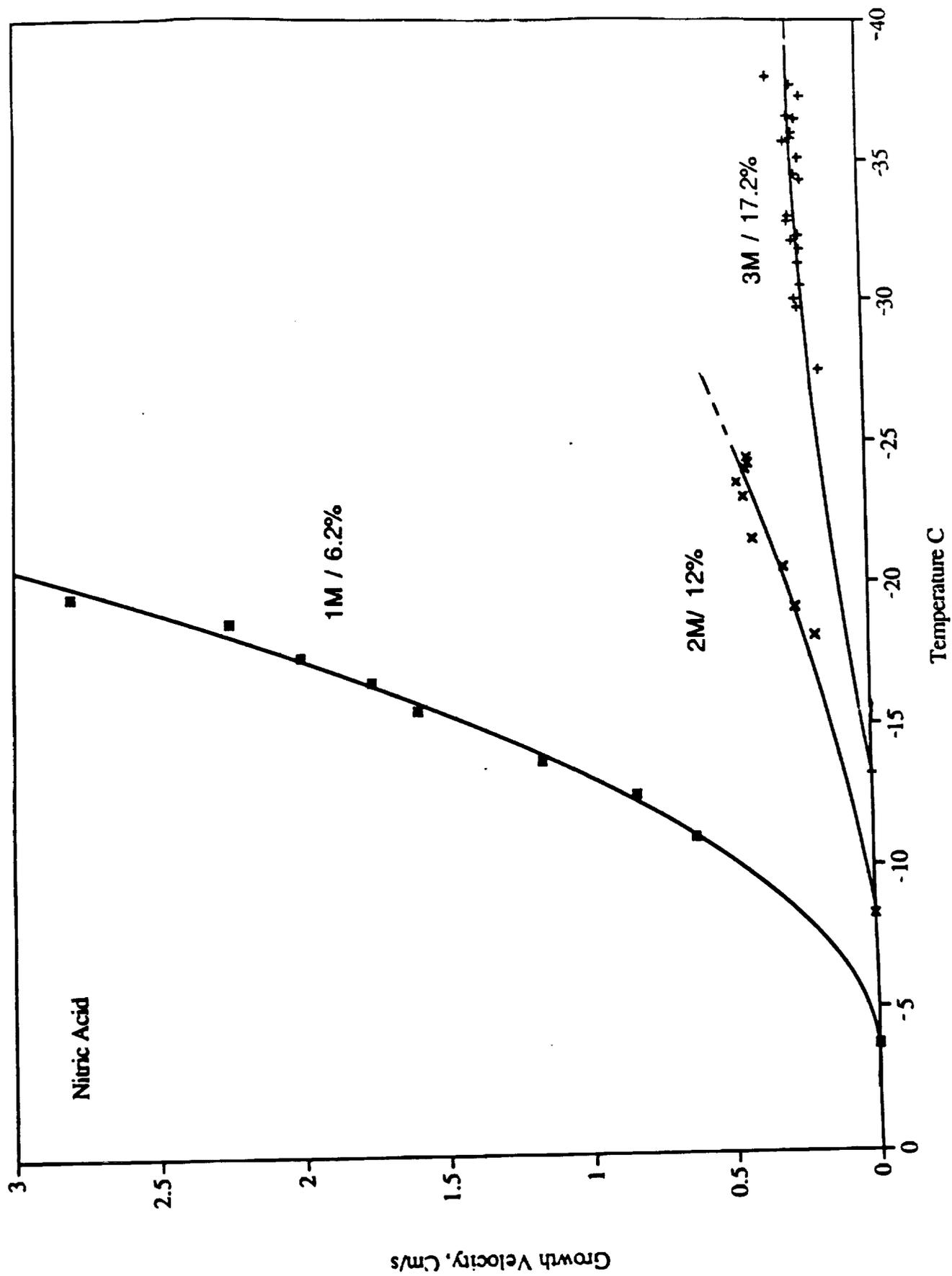


Fig. 11: Crystallization velocity of ice in nitric acid solutions of indicated molality, and composition by weight and temperature.

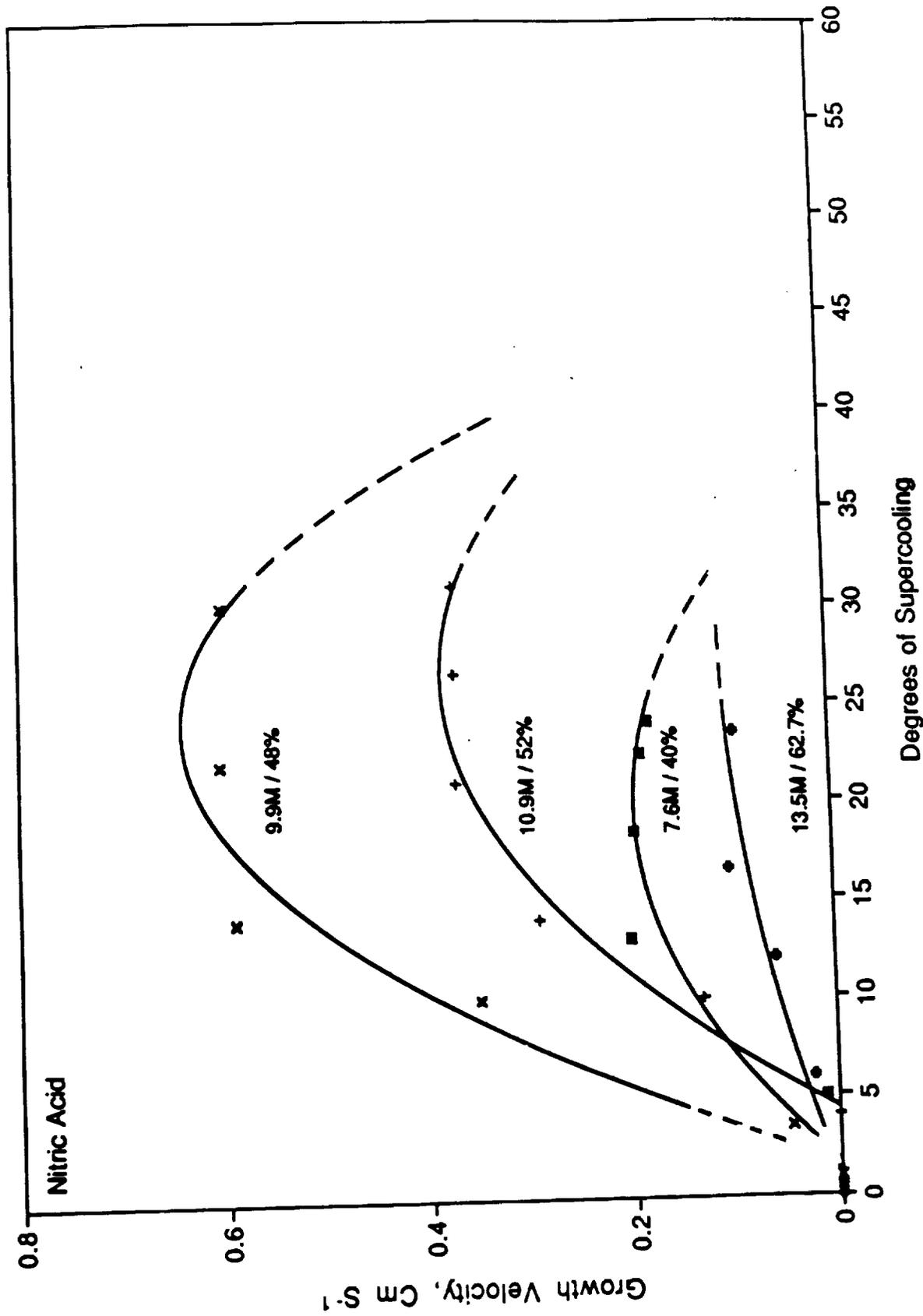


Fig. 12: As figure 11, plotted on an extended scale against supercooling.

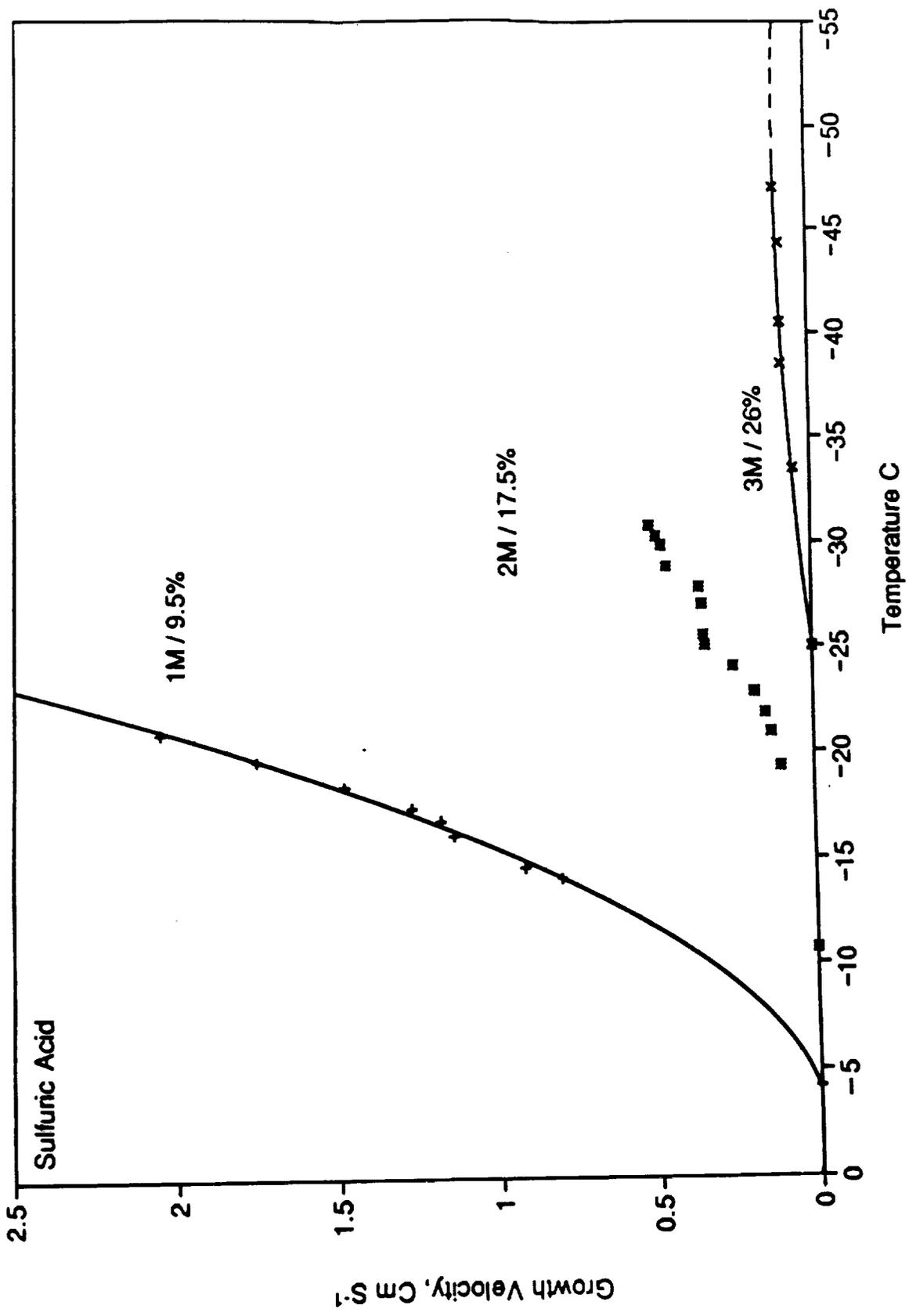
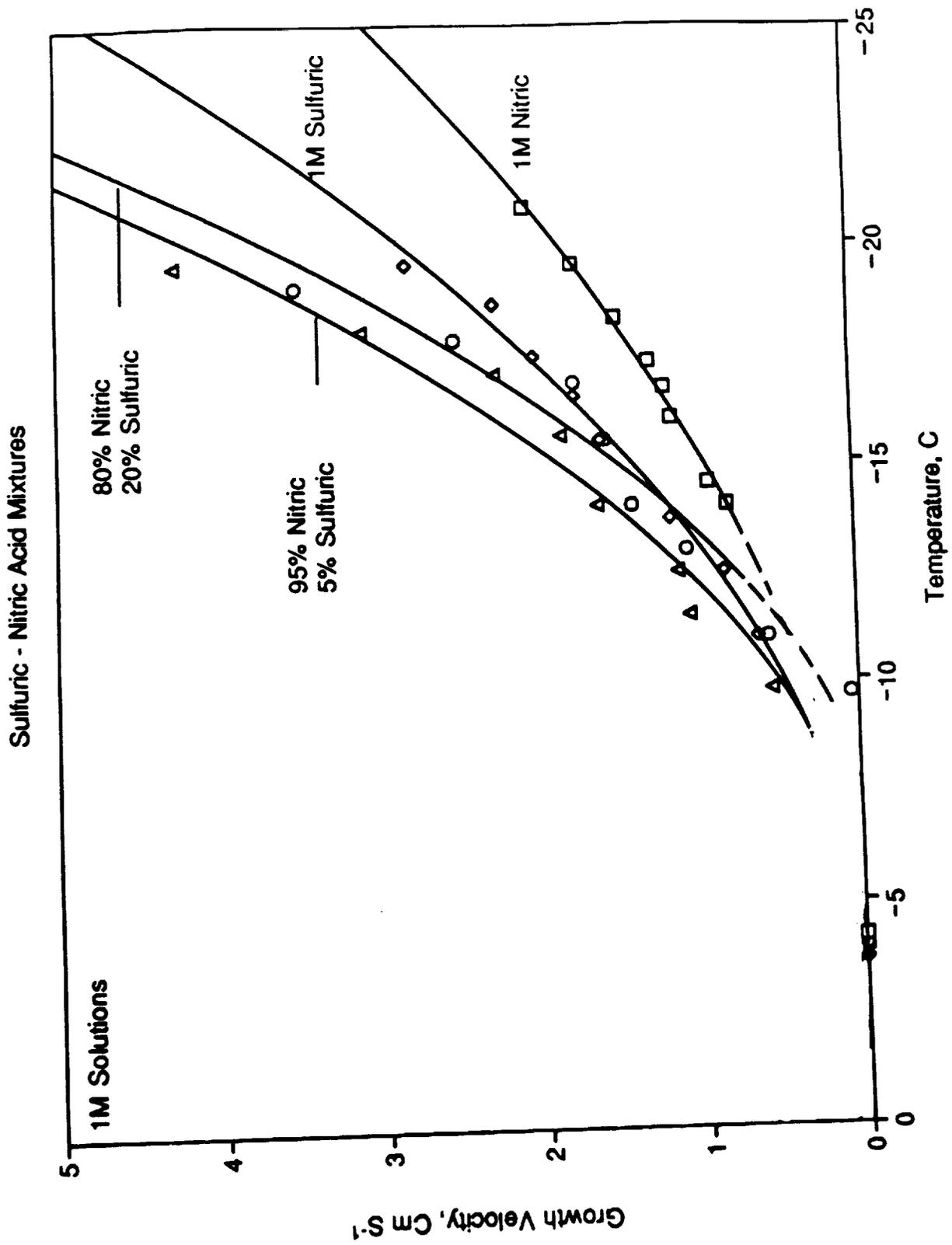


Fig. 13: As figure 11 for sulfuric acid.



**Fig. 14:** 1 m mixtures of nitric and sulfuric acid show enhanced velocities compared with individual solutions at the same molality.

Sulfuric - Nitric Acid Mixtures

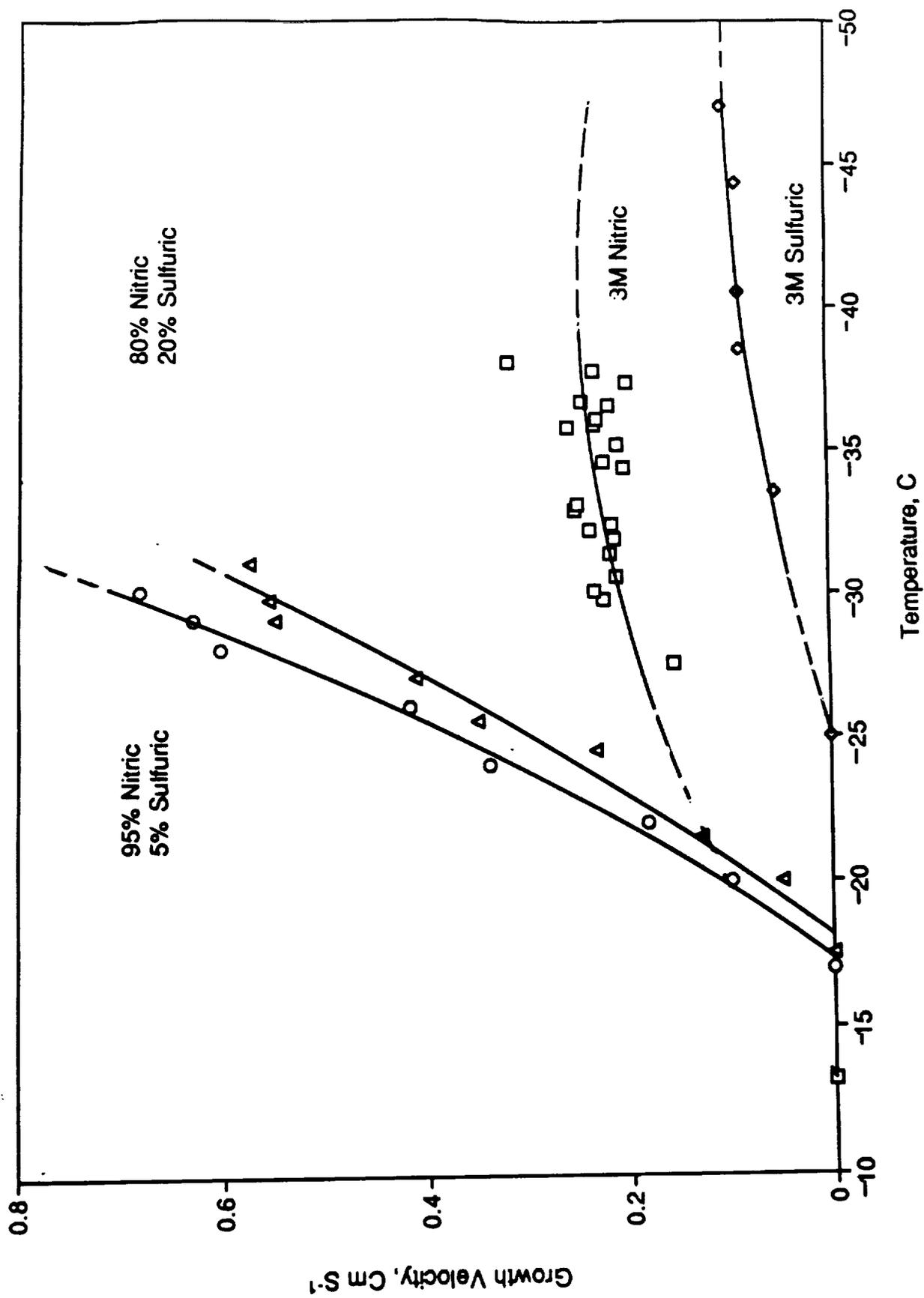


Fig. 15: As figure 14 for 3 M showing a greater relative increase of crystallization velocity.

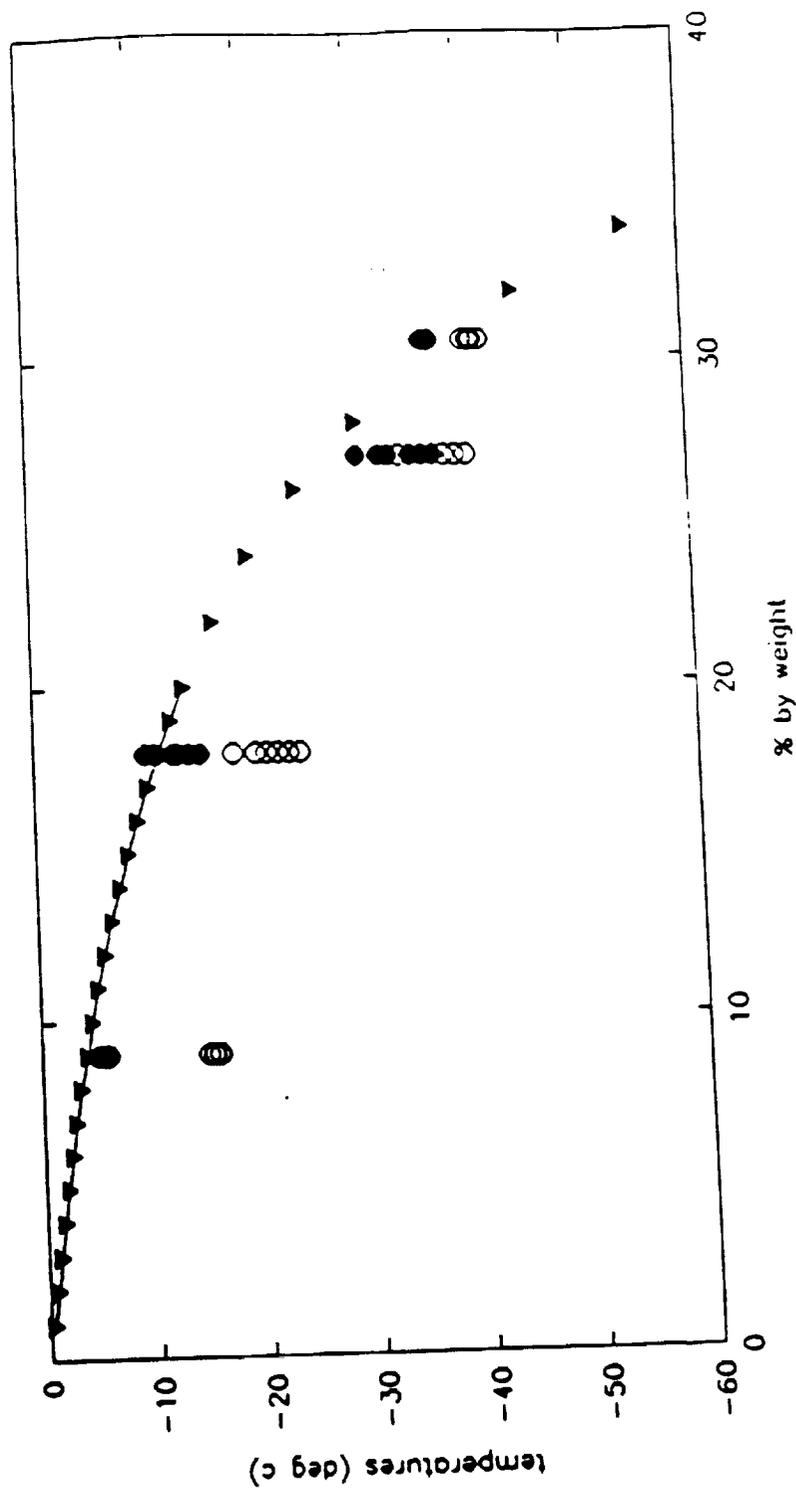


Fig. 16: Experimental data for equilibrium freezing point (solid circles) and maximum supercooling (open circles) for increasing molality and known data from the Chemistry-Physics handbook (solid triangles) for ice-solution equilibrium point for  $H_2SO_4$ .

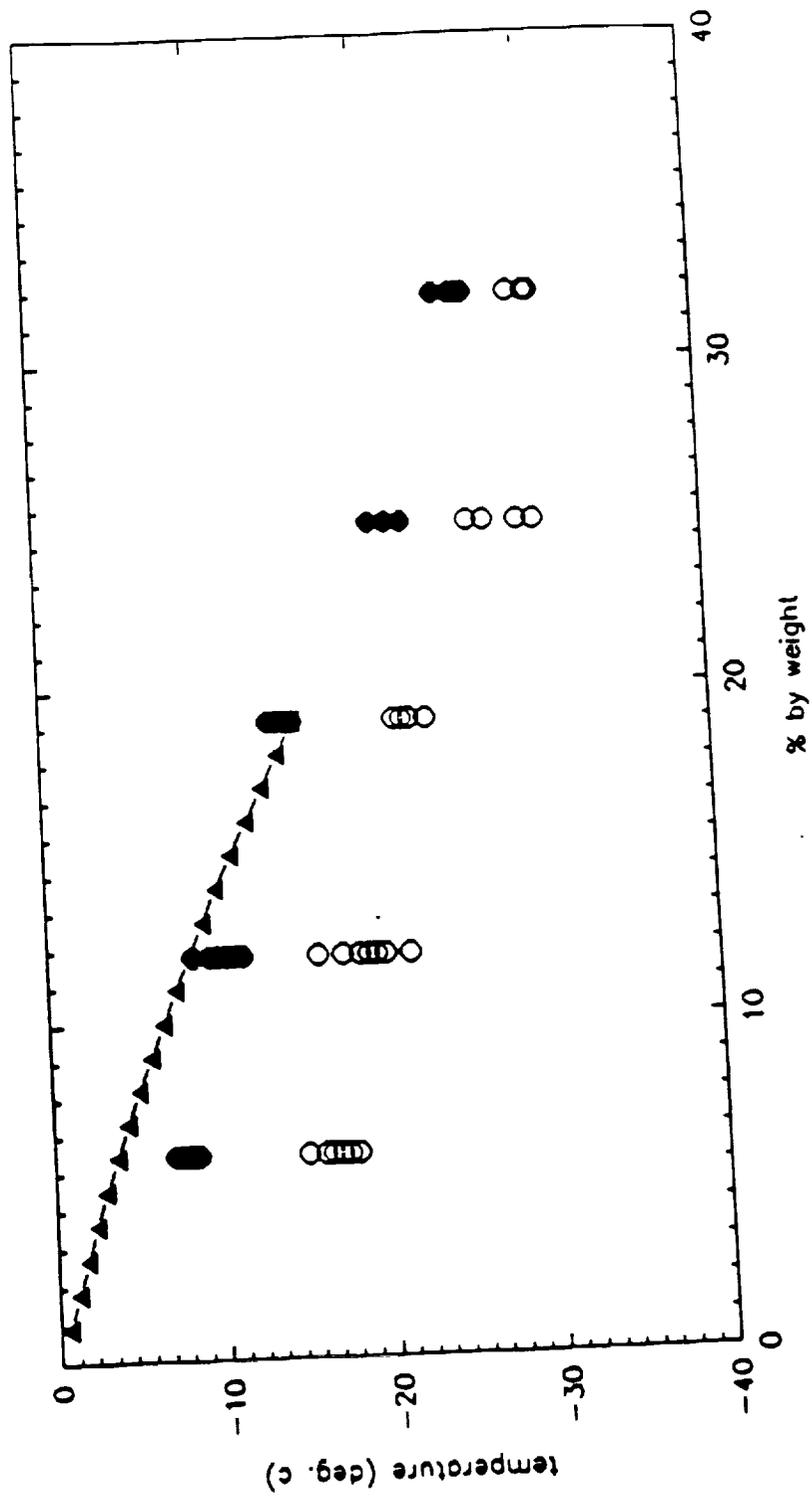


Fig. 17: As figure 16 for HNO<sub>3</sub>.

Sulfuric - Nitric Acid Mixtures

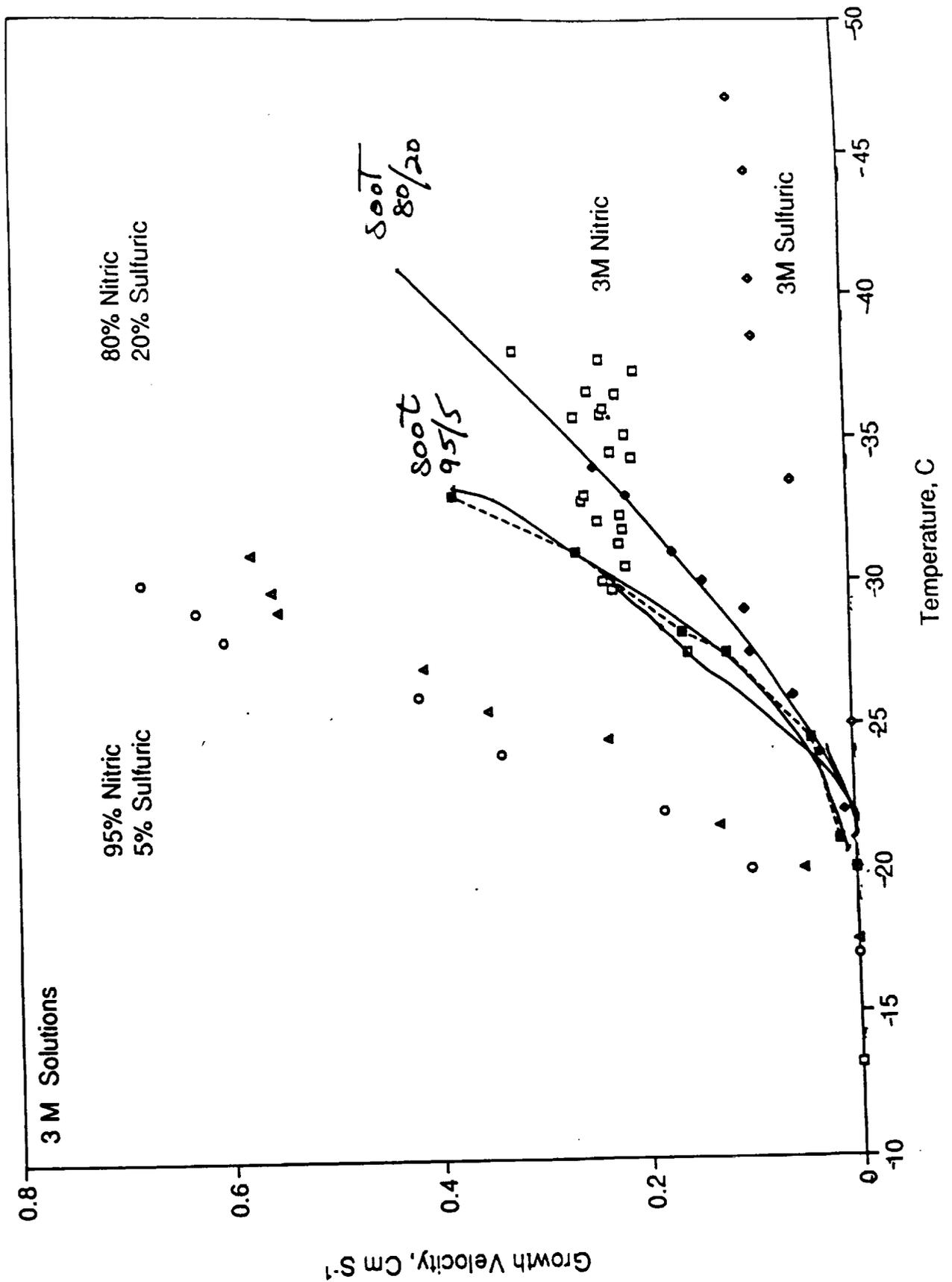


Fig. 18: Influence of soot from tail pipe of the Blackbird aircraft on growth velocity of ice in HNO<sub>3</sub> - H<sub>2</sub>SO<sub>4</sub> mixtures. There is an increase of the minimum supercooling by about 5° K, and also a reduction of growth velocity.

#### 4. Crystal Growth from the Vapor

General Considerations: when snow crystals grow in the atmosphere, the observed external form of the crystals is generally hexagonal, the habit (ratio of a/c axis) and the degree of completion of faces (dendritic or needle crystals compared with plates or columns) depends critically on temperature, supersaturation and fall velocity (Hallett, 1987). Whilst at low supersaturation (few %) the habit of ice crystals may be determined by the presence of emerging dislocations in preferred directions, under most atmospheric conditions, where the saturation is close to water saturation, growth is determined by surface nucleation and layer spreading and the habit by differential effects on planes perpendicular to a and c axes. Laboratory experiments (Keller and Hallett, 1982; Alena and Hallett, 1987) have shown that transition from plate to dendrite, and column to needle can be initiated by increase of ambient air velocity as well as increase in supersaturation. This occurs in practice as the fall velocity of a crystal exceeds a critical value, or, in the case of a frost crystal, as the surface wind speed exceeds a similar value. Experiments under low g were undertaken to investigate whether changes could be achieved by completely removing any ventilation (Alena et al, 1990). This showed a 20% reduction of growth rate from low g compared with slightly enhanced growth velocity with natural convection under 1 and 2g.

The nominal growth rate for an ice crystal under static conditions is given by;

$$\frac{dm}{dt} = \rho_i 4\pi r^2 \frac{dr}{dt} = \frac{4\pi C \sigma}{\frac{RT_\infty}{e_{sat}(T_\infty)DM_w} + \frac{L_s L_s M_w^{-1}}{KT_s RT_\infty}} \dots\dots\dots 2$$

where C is the electrostatic capacitance of the crystal (= radius for a sphere) and other symbols have their usual meaning (Pruppacher and Klett, 1980, p. 448). Thus the growth rate can be increased with supersaturation  $\sigma$ , and by increase of D and K. In air at 1 atmosphere at  $-10^\circ\text{C}$  the two terms in the denominator are almost equal; at higher levels in the atmosphere, the diffusion term dominates, until the two terms are again equal at 8 mb and  $-55^\circ\text{C}$  (Fig. 19). Thus for cirrus under crystal growth conditions the diffusivity term dominates.

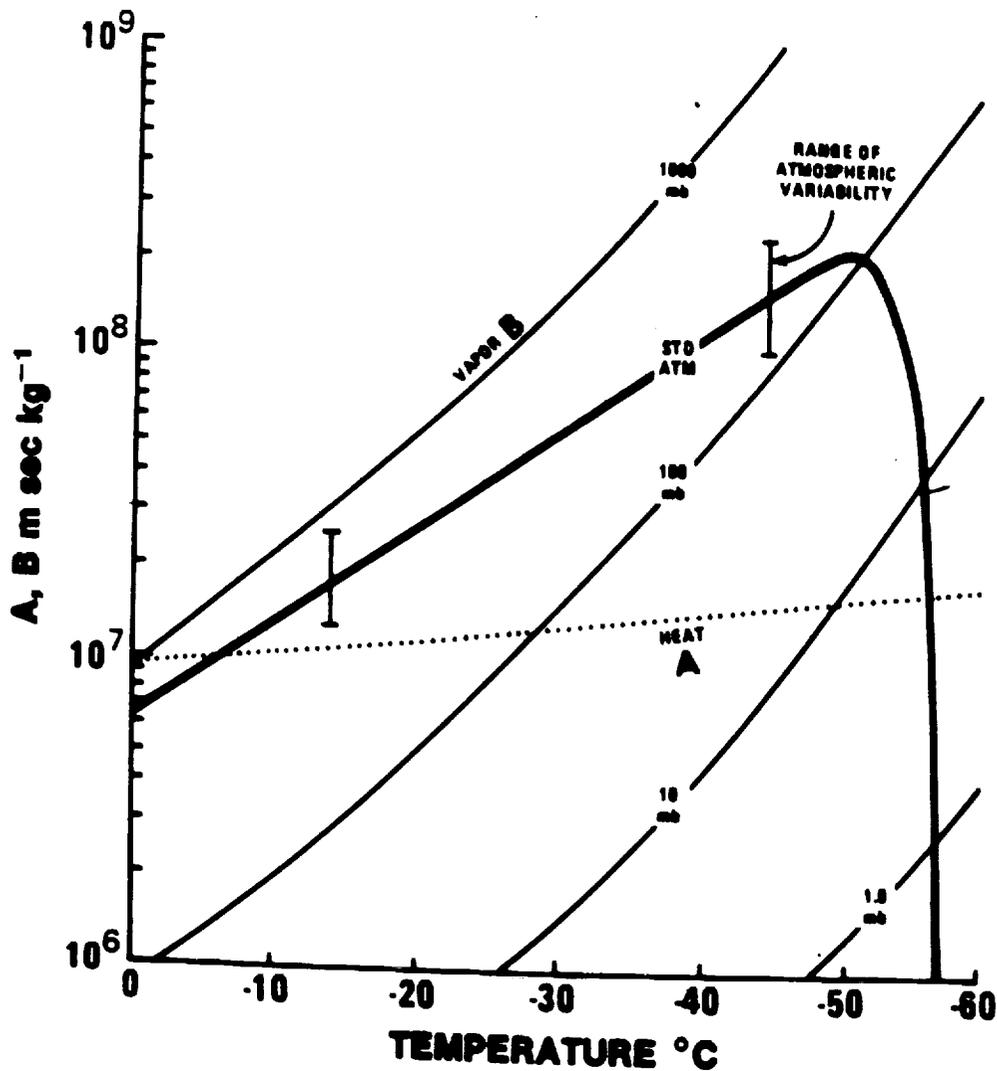


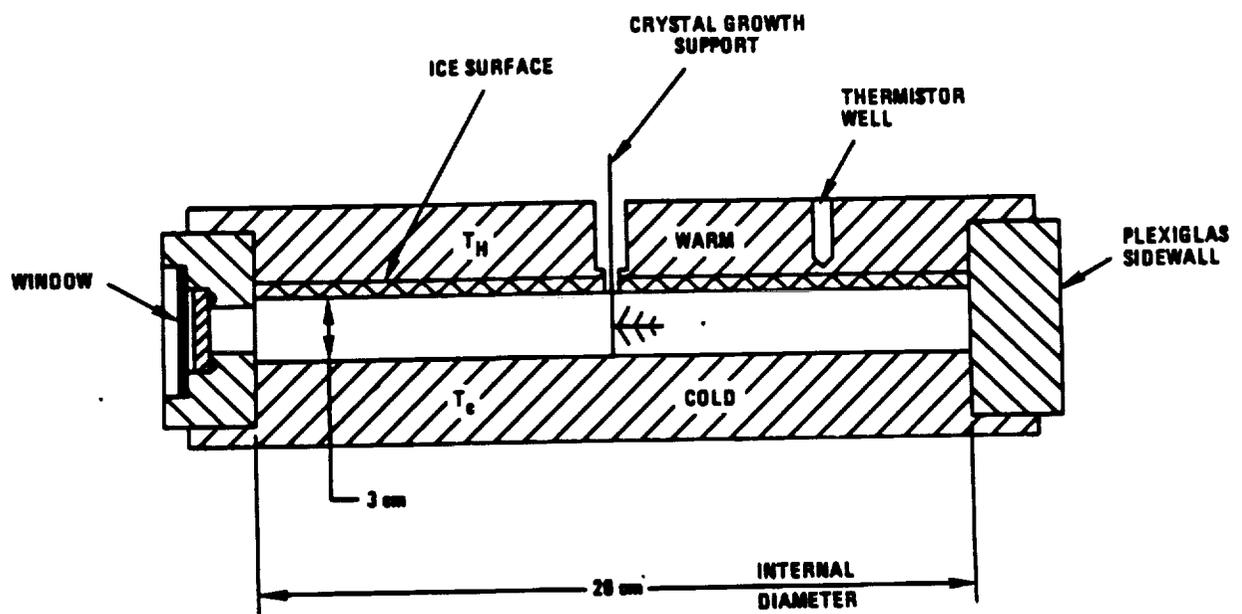
Fig. 19: Influence of temperature and pressure on the heat conductivity term (A) and vapor diffusivity term (B) for ice crystal growth under different conditions. The range of atmospheric variability of the diffusivity represents departures from the standard atmosphere. The diffusion term dominates for growth of cirrus.

This analysis is applicable to a crystal with uniform surface conditions; in practice this is far from the case as different facets of the crystal are subject to different local supersaturation, since different facets show different kinetics. The result is that a crystal grows in a dendritic or needle (non-faceted) shape where the local supersaturation is greatest and where faceted and layer growth give way to continuous growth on a molecularly rough surface. A thinner crystal (for heat and moisture transport reasons) grows faster. A little work has previously been done under simulated cirrus conditions. Kobayashi (1965) showed that in the temperature range  $-80/-90^{\circ}\text{C}$  ice crystals grew as thin needles, although supersaturation was not well controlled in this study.

## 5. Chamber Design and Construction

The static diffusion chamber is formed by two flat stainless steel plates 28 cm in diameter, spaced 3 cm apart, as shown in Fig. 20. A stainless steel porous wicking material is diffusionally bonded to the top surface to act as a water source. This wick is 0.1 cm thick, with a capacity of at least  $0.07\text{ gm/cm}^2$  of water. The chamber sidewall is constructed of a thick ring of plexiglass. Machined into the sidewall are two access ports, three gas ports, and two window openings. Windows are double pane to minimize heat transfer to the environment. Dry air is circulated between the windows to prevent any water vapor condensation that would impede viewing. The chamber can be flushed, evacuated and filled with other gases or aerosol. A glass fiber (1/2 mm diameter) with micrometer control of vertical position and rotation is inserted in the top center of the chamber to serve as a nucleation site for ice crystals. Crystals are viewed through a camera window  $2 \times 7\text{ cm}$  of optical crown glass, treated with a non-reflective coating.

The thermal plates are independently controllable through a temperature range from ambient to  $-80^{\circ}\text{C}$ . Each 2.5 cm thick stainless steel plate has a 0.5 cm thick copper disc brazed to the surface opposite the inside surface. The copper is intended as a thermal buffer to achieve uniform temperatures in the thermal plate. An insulation package equivalent to at least 5.0 cm of air surrounds the chamber to reduced the effects of heat transfer from the environment.



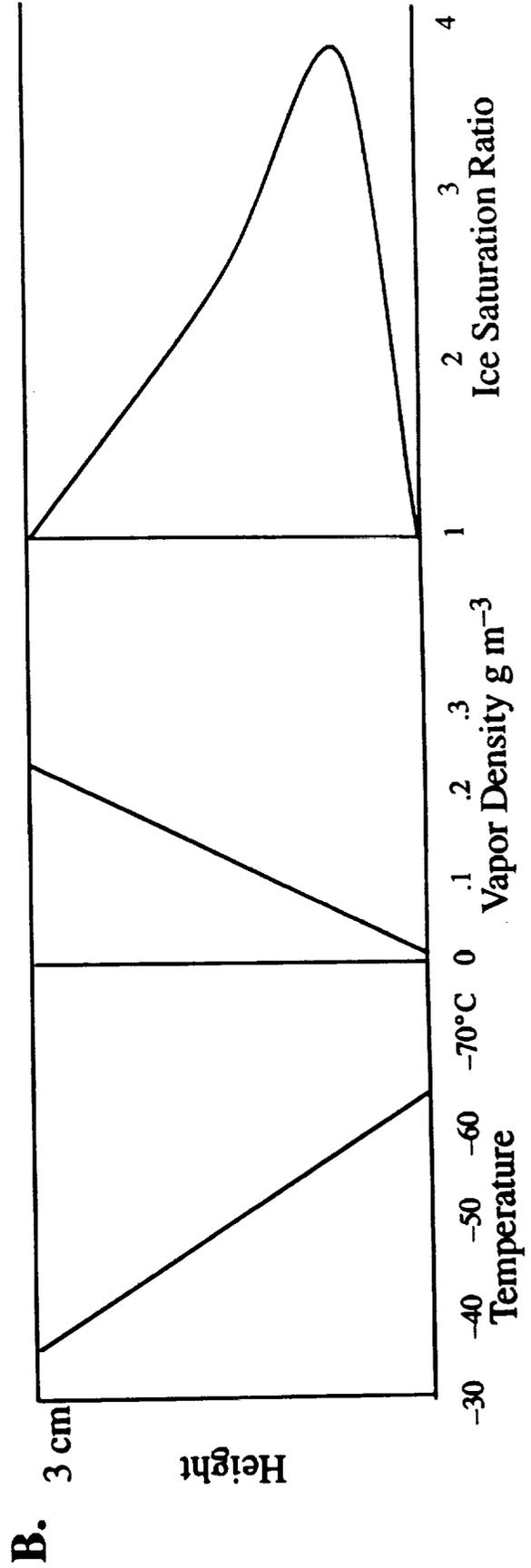
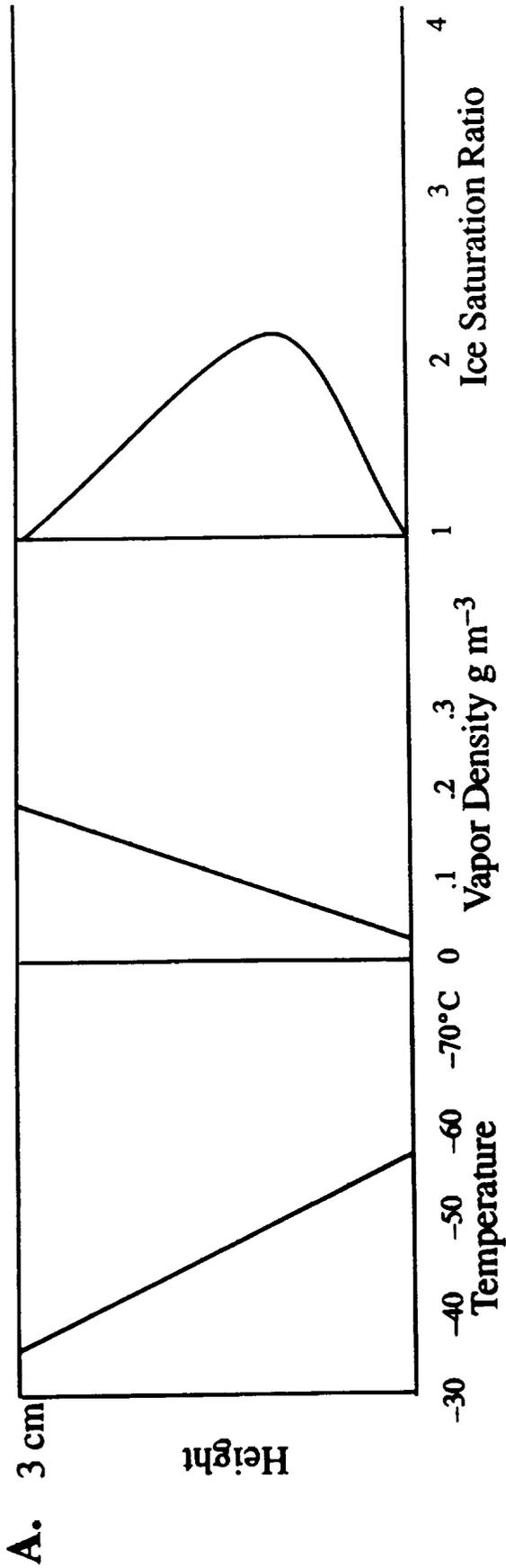
**Fig. 20:** Cross section of the static thermal vapor diffusion chamber for ice crystal growth in air under cirrus conditions (100-200 mb, -30 to -60° C).

The diffusion chamber cooling was modified to provide lower temperatures by use of a 2 stage compressor refrigeration system. This was circulated to the "warm" thermoelectric side, and the temperature of the plate controlled by a feedback system with thermocouple input to power the thermoelectric systems. This enabled temperature to be selected to about  $\pm 1^\circ\text{C}$  and controlled to an accuracy of about  $1/2^\circ\text{C}$ .

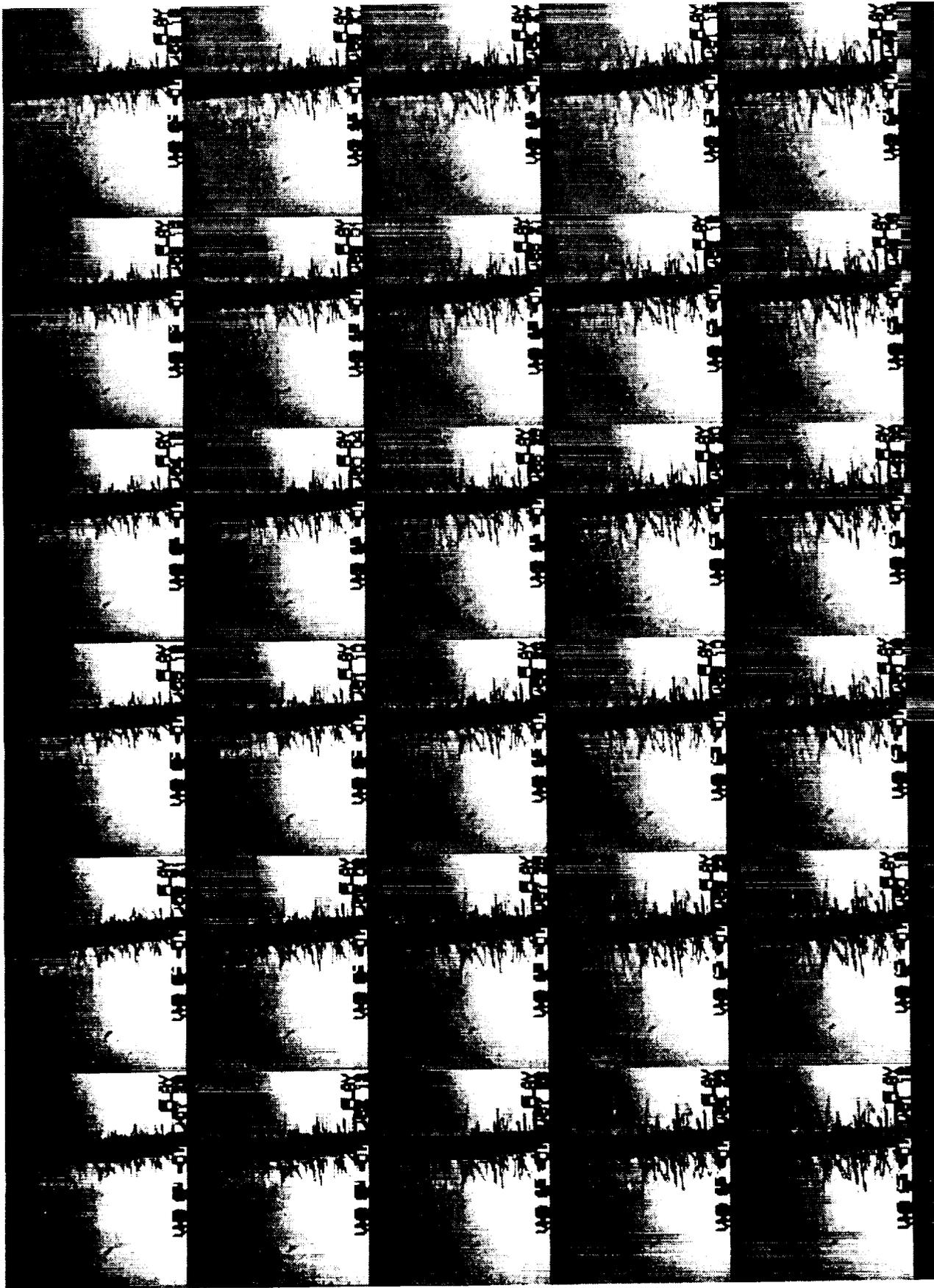
It had originally been intended to introduce water to the upper plate by use of a reservoir and feed. This gave problems by unknown water distribution and dripping to the lower plate. The procedure adopted was to flood the lower plate with about 2 mm of water, evacuate the chamber to 1/100 atmosphere, and cool the top plate to  $+5.0^\circ\text{C}$ , leaving the base plate at room temperature. The water condensed on and was absorbed by the top plate until it appeared visually wet. The pressure was returned to ambient, the lower water drained, and the plates cooled to the required value. The pressure was set for an appropriate level (10-200 mb) and after a 'rain out' period for nuclei in the original air ( $1/2$  hour), the fiber was lowered allowing crystals to grow. The run was limited by evaporation of the ice from the top plate which took several hours under the simulated cirrus conditions. Figure 21 shows the ice vapor density, temperature and supersaturation profiles computed assuming a linear profile from measured top and bottom temperatures, these surfaces assumed to be saturated at their respective temperatures.

Figs. 22, 23 show the form of crystals for these two runs, as thin columns. There is a tendency for greater growth rates towards the lower parts of the photographs, consistent with the increased supersaturation shown in Fig. 21. Linear growth rates of the columns can be measured (Table 1). The center location, in each sequence is near the chamber center. The enlargements of Fig. 24 show that the tip of each column is somewhat rounded, but the width of each column is constant over most of its length at  $60 - 80 \mu\text{m}$ , and does not vary significantly with ambient supersaturation.

It is pointed out that cirrus crystal simulation does not include ventilation (as in the original Keller and Hallett, 1982 work) as it was not practical to operate the present chamber under ventilation. The ventilation effect on growth rate can be approximated by considering an



**Fig. 21:** Temperature, vapor density and ice supersaturation for intermediate (A) and high (B) supersaturation chamber runs for growth of ice crystals simulating cirrus conditions.



c. 70

Fig. 22: Sequential digitization of images showing growth of columnar crystals, under conditions shown in Fig. 21. The vertical extent of the images is about .75 cm near the chamber center. This is where the supersaturation is increasing from top to bottom. Temperature  $-7^{\circ}\text{C}$ ; ice saturation ratio 1.7. Frame intervals about 1 minute.

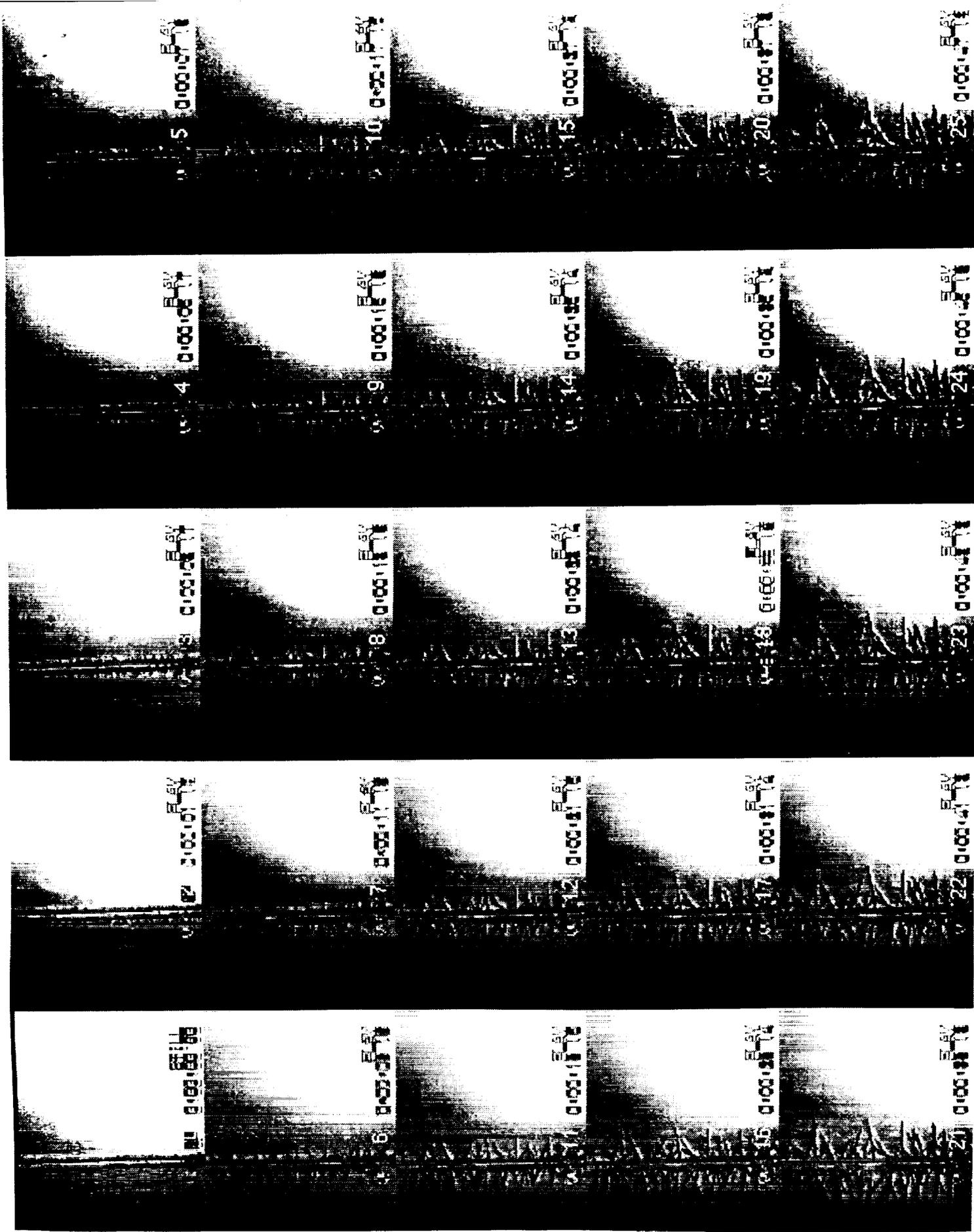


Fig. 23: As figure 22, central temperature  $-45^{\circ}\text{C}$ ; ice supersaturation 2.5, sequence B, figure 21. Note that figure 22 is enlarged compared with figure 23.

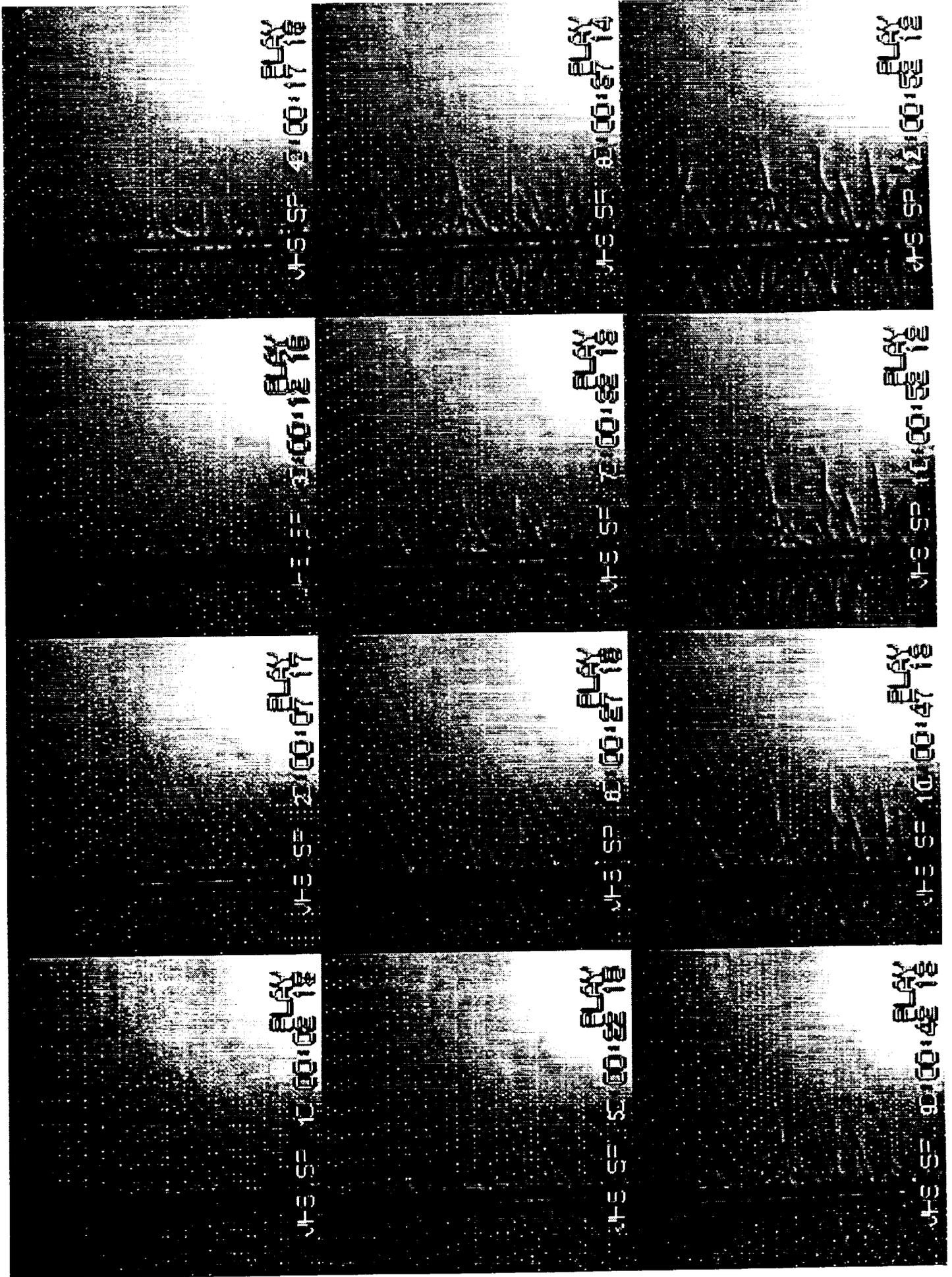


Fig. 24: Enlarged sections at 5 minute intervals, sequence A.

additional term in equation 2 (page 28):  $[1 + 0.23 (\text{Re})^{1/2}]$  where  $\text{Re}$  is the Reynolds number at the terminal fall velocity. Taking  $V = 50 \text{ cm s}^{-1}$   $d = 250 \text{ }\mu\text{m}$ ,  $\nu = 2 \text{ cm}^2 \text{ s}^{-1}$  (all generous estimates), this gives an enhancement of some 10% which is not significant in carrying the present experiments over to the atmosphere. The two runs give two different saturation ratios equivalent to a doubling of supersaturation. Thus the growth rates are approximately proportional to the supersaturation, to the accuracy of the measurements in these two runs. Further experiments are underway to investigate habit at smaller supersaturation. There is evidence that at well below water saturation (less than half way between water, and ice saturation), growth again occurs as thin plates (Keller et al 1980). The observation of plates at low temperatures in Antarctica and in cirrus cloud confirms this possibility (see photos in W. Tape, 1995). Observations of crystal habit at known temperature therefore can be used to infer within certain limits to the ice supersaturation under which growth took place.

<b>Table 1: Linear Growth Rate Characteristics of Columnar Crystals</b>			
	Linear growth rate $\mu\text{m s}^{-1}$	Range of Saturation Ratio over Ice	Temperature Range and Mid temperature
Run A	$0.78 \pm .2$	1.4 to $2.1 \pm 0.1$	-45, -49°C -47 $\pm \frac{1}{2}$ °C
Run B	$1.7 \pm .30$	2.2 to $2.9 \pm 0.1$	-42 -49°C -45 $\pm \frac{1}{2}$ °C

## 6. Conclusions

Three specific studies have investigated properties of hygroscopic substances important in high level clouds in the atmosphere. The important findings are:

- Substantial supersaturation of solutions of soluble compounds are likely to occur under atmospheric conditions. This study shows supersaturations of 150%; higher supersaturations are likely in smaller particles. The results are in general agreement with suspension experiments (Tang and Munkelwitz, 1977, 1984; Tang et al 1978). The new results suggest an inhibition of crystallization rate under high supersaturation for larger concentrations.
- Substantial supercooling of solutions of soluble compounds and acids occur in volumes about 1 to 0.01 ml; substantially greater supercooling is anticipated in smaller volumes as in haze droplets  $10^{-10}$  to  $10^{-15}$  ml.
- A technique has been devised to study the forms of ice crystals growing over the range of cirrus temperature. Two experimental runs show growth as long thin columns over this temperature range at moderate to large supersaturations. The shape of the crystals has implications for optical properties, as long thin crystals behave differently in scattering magnitude and phase (angular dependence) in comparison with spheres. A question arises as to whether such particles can grow long enough to orient by hydrodynamic effects in fall or in local electric fields. The shape of observed crystals may be utilized to infer supersaturation for growth at a known temperature.
- The technique is now capable of producing PSC crystals with nitrate. It will be necessary to use nitric acid solution and transfer it to the top plate by a method similar to water vapor. This will require using a lower base temperature (not possible in this study) to reach a lower central temperature where nitrate hydrates form (below  $-95^{\circ}\text{C}$ ). This can be achieved by use of a lower temperature cooling for the thermoelectric elements, by means of a more thermally efficient direct refrigerant cooling coil rather than using an intermediate fluid for heat transfer.

## 7. Implications

The existence of solutions with increasing viscosity at higher concentration and lower temperatures implies a lowering coefficient of diffusion, Water has values about  $10^{-4}$ ; a glass approaches  $10^{-12}$   $\text{cm}^2 \text{s}^{-1}$ , comparable with a solid. For a particle size  $1 \mu\text{m}$ , the time for significant diffusion is of order  $r^2/D$ . This gives  $10^{-4}$  s for a water drop and  $10^4$  s for a glass or ice particle. Thus clouds with life times of  $10^3$  s (as evolving cirrus) surface adsorbed reaction times are important for ice and deeply supercooled/supersaturated particles; for water drops and dilute solutions diffusion throughout the volume occurs readily. The surface reaction rate processes take place in series with the rate processes described here and the totality must be described for the complete theory of the reactions.

This study also investigated the occurrence of nuclei which apparently enhance slightly the supercooling and supersaturation. This is a strange effect and may result from dissolution of 500+ components to inhibit pre-existing nuclei. The combined effects of solution mixtures on growth rates requires further evaluation, solution studies from soot collected on the Blackbird engine showed some effect for the substances as tested.

The overall implication is that particles present at cirrus and PSC levels are capable of existing in a metastable condition, that it is difficult to predict this, and it may have significant effect on optical properties and chemical reaction rates through particle shape and internal diffusion rates.

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## **9. Publications and Presentations Resulting from NASA Grant No. NAG-W-2572**

Teets, E. and J. Hallett, 1992: Nucleation and Crystallization of Highly Supercooled and Supersaturated Stratospheric Aerosol. 1992 AGU Fall Meeting, December 7-11, San Francisco, California.

Hallett, J., 1994: Cirrus Ice Crystal Nucleation and Growth. AMS Eighth Conference on Atmospheric Radiation. January 23-28, 1994, Nashville, Tennessee. Conference Proceedings, 220-221.

Hallett, J., J. G. Hudson, B. Queen and E. Teets, 1995: Aerosol and Cirrus Opacity. Paper No. AIAA 95-0544, 33rd Aerospace Sciences Meeting, Jan. 9-12, 1995, Reno, Nevada

Queen, B., E. Teets and J. Hallett, 1995: Supercooling and Glass Transition of Aqueous Solutions at High Concentration. To be published.

Queen, B., 1995: Crystallization of Highly Supersaturated Aerosol. M.S. Thesis, Univ. of Reno, Nevada.

Teets, E., 1995: A Laboratory Study on the the Phase Transmition for Polar Stratospheric Cloud Particles. M.S. Thesis, Univ. of Reno, Nevada.

Hallett, J., 1995: Crystal Growth from the Vapor at Cirrus and Polar Stratospheric Cloud Temperatures. In Preparation.

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**AIAA 95-0544**

## **Aerosol and Cirrus Opacity**

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**33rd Aerospace Sciences**  
**Meeting and Exhibit**  
**January 9-12, 1995 / Reno, NV**

# AEROSOL AND CIRRUS OPACITY

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## 1. INTRODUCTION

Hygroscopic aerosol present in the earth's atmosphere takes up and loses water depending on relative humidity, broadly described by the Köhler Equation. As relative humidity increases from a low value, any hygroscopic particle takes up water vapor, forming a solution whose concentration decreases with growth. A soot particle with a hygroscopic component may reside within the drop or at the surface; its optical, absorption - scattering properties depend on the geometry (Chylek and Hallett, 1992). Should the relative humidity decrease, the droplet evaporates. In the situation where the hygroscopic component was crystalline, significant supersaturation may occur; the degree of supersaturation depends on the presence or absence of appropriate nuclei. In situations where the temperature falls below the equilibrium melting point depression of the solution,  $1.86iM^{\circ}C$  ( $i$  = activity coefficient  $M$  = molality), nucleation may occur, and crystals of ice or a hydrate may grow, depending on solution composition. In the lack of nucleation, substantial supersaturation may occur, leading to liquid phase droplets at temperatures down to below  $-80^{\circ}C$  (Hallett and Lewis, 1967; Ohtake, 1992).

A large unknown is the role of insoluble particles on solute and hydrate nucleation. The action of particles isomorphous with ice is somewhat

understood; mineral particles (clays) are of importance, as well as organic materials and some bacteria (*Pseudomonas Syringae*). The extensive occurrence of supercooled water clouds at mid tropospheric levels points to the ineffectiveness of transport of such particles to these levels; the occurrence of supercooled lenticular water clouds at temperatures approaching  $-35^{\circ}C$  provides similar evidence (Heymfield to Miloshevick, 1993). At temperatures below  $-35/-40^{\circ}C$  for pure water or at these temperatures below the equilibrium melting point for solutions, homogeneous nucleation takes place. A question arises as to the effect of soot from aircraft exhausts. It appears that the nucleation properties of some soots are minimal (Hallett et al 1986; DeMott, 1990), consistent with a lack of crystalline structure. Even so, small insoluble particles (even of non crystalline form) might be expected to lead to nucleation at temperatures higher than that required for homogeneous nucleation.

## 2. NUCLEATION PROPERTIES

The CCN spectrum and CCN/CN ratio of aircraft soot gives insight in how this interaction occurs. Measurement of the CCN spectrum of soot during flight behind different jet aircraft shows that only a few percent of soot particles are significantly hygroscopic to be active at 0.8% supersaturation, (Pitchford, Hallett and Hudson, 1991). Figure 1

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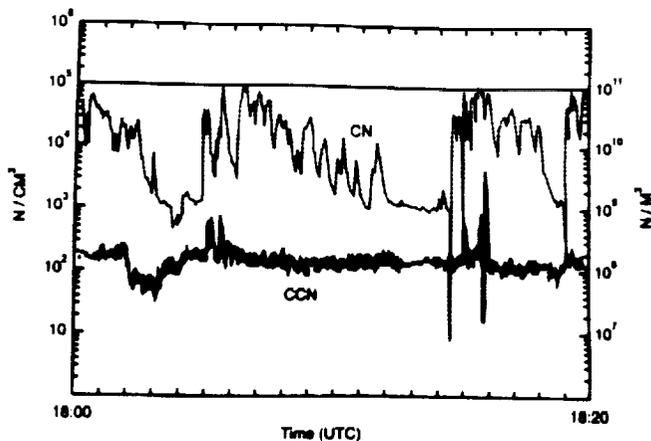


Figure 1. Total nuclei (CN) measured by a TSI 3020 counter and Cloud Condensation Nuclei (CCN) measured in a spectrometer, active at 0.8%. Measurements were made in the trail of a jet aircraft some 5 km distant.

shows measurements taken from a chase aircraft some 5 km behind the lead aircraft. CN (total nuclei) is measured by a TSI 3020 and CCN by a DRI spectrometer. The same lack of activity is true for smoke from "sweet" crude oil, (Hallett et al 1989), although sulfur containing crude is much more active.

### 3. LABORATORY STUDIES

The supercooling/supersaturation of solutions important under atmospheric conditions may be studied in the laboratory. Small (0.1 ml) quantity of solutions in a narrow glass tube or as a drop 0.01 ml on a hydrophobic substrate may be supercooled or

supersaturated and the extent of supercooling or supersaturation and the crystallization characteristics examined. Two distinct approaches are necessary. For ice or hydrate nucleation solution of a known concentration, a ½ mm diameter tube is slowly cooled until nucleation occurs spontaneously, or nucleation is triggered by a LN<sub>2</sub> cooled wire at the surface of the solution. The crystallization is viewed by video, and a linear crystallization velocity measured. These velocities can be mapped as a function of supercooling and concentration for each material. Substantial supercooling (> 20°C) can be achieved by this technique. For crystallization of solutes, a different technique is required. The cooling of solute below its equilibrium in contact with glass surfaces is a difficult technique - it appears that dried solution creeping along the wall by capillarity, or defects in the glass act as nucleation sites at only small supersaturation. An alternative technique utilized humidification of a small crystal (100 µg, pre-weighed) on a fresh polyethylene surface, such that dissolution was complete. The drop is viewed from the top and side simultaneously. As the drop is subjected to lower humidity, it evaporates slowly at a rate such that the internal gradient of composition is minimal. Nucleation and crystal growth is video recorded. The concentration of the solution is calculated from the initial crystal mass and the volume of the cap. In this case, the crystallization velocity can be mapped as related to concentration and supersaturation. The technique is evidently not appropriate for substances which are not available as small crystals to permit an initial weight determination. Fig. 2(a, b, c and d) show results for ice crystallization of nitric and sulphuric and (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub> and (NH<sub>4</sub>) HSO<sub>4</sub> solution; Fig. 3(a and b) show solute crystallization of (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub> and (NH<sub>4</sub>) HSO<sub>4</sub> solution. These graphs show that in the solutions studied, as high concentration is approached, the crystallization velocity is lower for higher concentration, as would be expected from mass transport considerations, and that there is a maximum in the crystallization velocity as the supercooling or supersaturation is increased. This strongly suggests that a glass transition may occur for even lower temperatures.

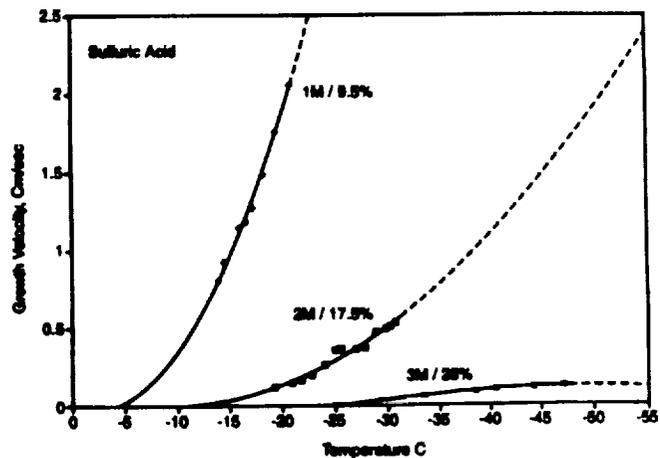
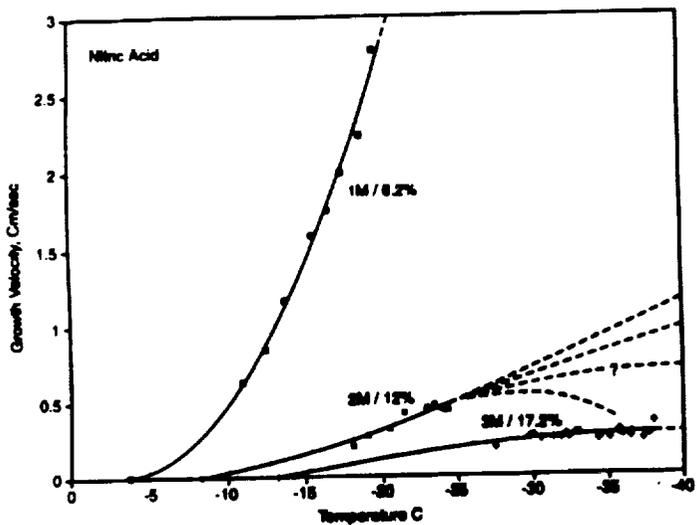
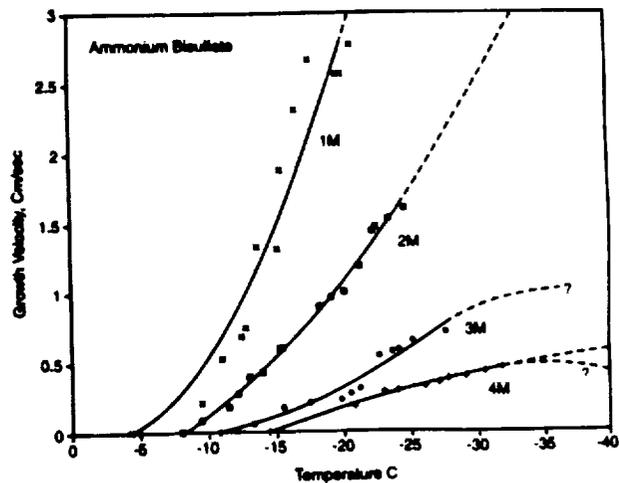
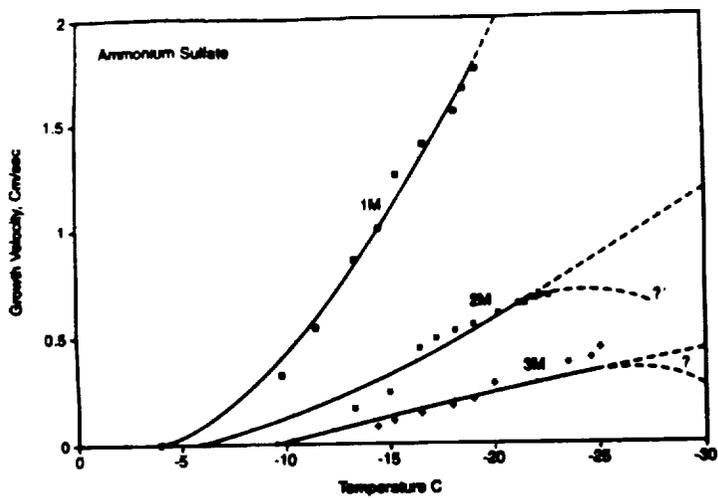
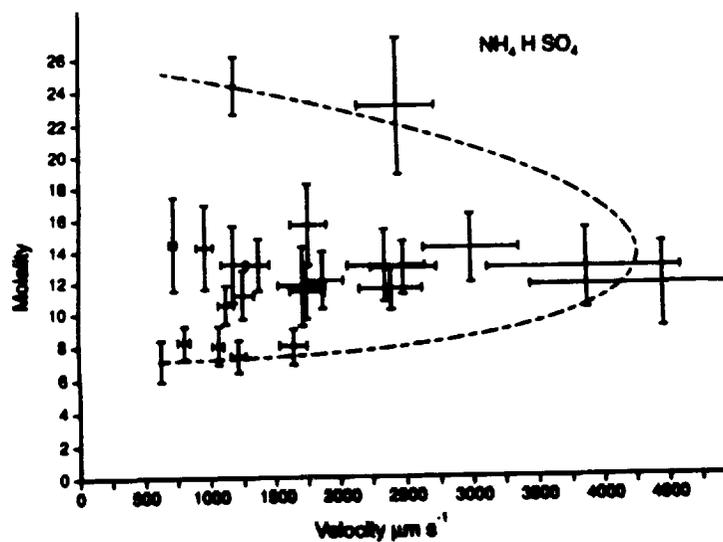
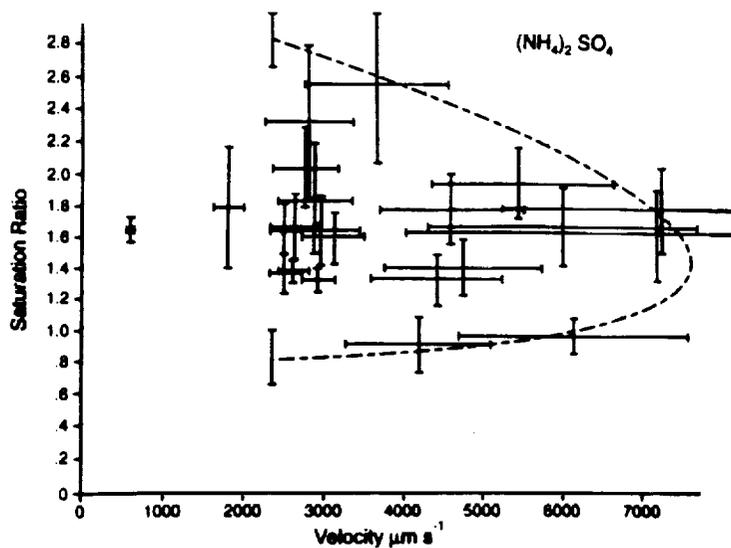


Figure 2. Crystallization velocity of ice in supercooled solutions. Lowering of rate of increase of crystallization velocity with increase of supercooling suggests approach of a glass transition.



**Fig. 3.** Crystallization velocity of solute in supersaturated solutions. The dashed line is an envelope of maximum growth velocities showing a maximum at a critical supersaturation. (Note:  $\text{NH}_4\text{HSO}_4$  is given as absolute molality as equilibrium data was not available).

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#### 4. APPLICATION

The implication of these observations to particles in the atmosphere is first to be related to the likely occurrence of these materials. It is known that nitrate (as hydrate) form at low temperatures in Polar Stratospheric Clouds (Dye et al, 1992); sulfuric acid may be present from oxidation of  $\text{SO}_2$  produced by industry, plant decomposition, and irregularly, volcanic activity such as Pinatubo, ammonium sulfate and bisulfate form neutralization by ammonia from biological sources. There is also evidence that nucleation of aerosol mostly of industrial origin at least under near surface conditions, is somewhat uniform (Rood et al 1989). There is evidence of visibility hysteresis with respect to relative humidity in coastal regions, with somewhat less solid particle aerosol. Of current interest is the potential role of aircraft soot, particularly that produced at high levels ( $-50^\circ\text{C}$ , 40,000 ft) which may be slightly contaminated with a sulfuric acid layer. The effects are to be compared with sulfuric acid droplets possibly formed on aerosol from volcanic aerosol, or *in situ* nucleation at these levels (Clarke, 1993). The presence of large numbers of particles capable of nucleation of ice particles at cirrus levels is of interest for two reasons: First, the emissivity, and optical depth of cirrus depend critically on the presence of large numbers of small particles. On occasion, these properties are dominated by particles of size 10 - 50  $\mu\text{m}$  (Arnott et al, 1994). There is observational evidence that volcanic produced aerosol give smaller and more numerous crystals (Sassen 1992). Second the occurrence of surface chemical reactions at these levels is predicated by absorbed reactions, and the presence of large numbers of small particles is conducive to these effects. Cirrus forms by cooling of air lifted through the  $-40^\circ\text{C}$  level and the occurrence of large numbers of small particles or a few large particles depending on the rate processes involved (Jensen and Toon 1994) and base temperature being above or below  $-40^\circ\text{C}$ .

Two extreme scenarios are of interest, slow updraft with cloud base temperature above  $-40^\circ\text{C}$  give a few large crystals, which fall out and redistribute

water substance downwards. Nucleation results from dilution and freezing of the long tail of the CCN spectrum. Other droplets may subsequently evaporate, to produce highly concentrated supercooled/supersaturated nuclei, which freeze only at much lower temperatures. Alternatively, the cloud base may be colder than  $-40^\circ\text{C}$  with stronger updrafts. Here a much wider tail of the CCN spectrum nucleates, to give a higher concentration of smaller frozen droplets, together with smaller number of liquid interstitial haze particles. The relevance of the occurrence of high supersaturation is now apparent; the occurrence of the glass phase essentially inhibits crystallization at low temperature and because of reduced internal diffusion, gives opportunity for surface reaction as already can occur on the crystalline particles.

#### 5. CONCLUSIONS

These considerations raise questions concerning the role of particulates injected into cirrus levels either naturally or by aircraft:

- The nucleation ability of soot particles on smaller particles and at larger supersaturation/supercooling than achieved in the above measurements.
- The supersaturation/supercooling expected for soot containing particles from the aircraft exhaust and during atmospheric processing in the aircraft wake.
- The activity of natural and aircraft contrail aerosol for the growth of droplets at cirrus level - the CCN/CN spectrum and their importance in cloud opacity.
- The role of solid supersaturated particles in heterogeneous chemical reactions at these levels.

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## CIRRUS ICE CRYSTAL NUCLEATION AND GROWTH

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### 1. INTRODUCTION

The ice which constitutes cirrus crystals can be expected to form from the remnants of vapor and possibly small particles which are left over from the precipitation processes responsible for removing water substance either in deep convective cloud systems - primary in the tropics but also in some mid-latitude summertime vigorous convection - or in mid-latitude frontal ascent. Thus, depending on the overall efficiency of the precipitation process, related to altitude and the associated temperature, cirrus formation may take place in air with dew point determined by its precipitation history, which may be substantially below  $-20^{\circ}\text{C}$ . Lifting which gives rise to the cirrus may originate in the deep convection itself or in shear anvils reinforced by local orographic or gravity wave effects. Widespread vertical ascent of frontal uplift and associated jet stream, possibly reinforced by orographic or other gravity waves also leads to cirrus. Thus one might expect that cirrus - as defined by a meteorological context - could form from air having a variety of dew points, to give ice crystals of sufficient concentration and size to fall into the cirrus classification.

### 2. Nucleation

From a knowledge of the nucleation characteristics of water droplets (cloud condensation nuclei) and ice crystals (from ice nucleation) we can argue that critical events might be expected to occur near  $-35/-40^{\circ}\text{C}$  where homogeneous nucleation of pure water

droplets happens; this mode always dominates over heterogeneous nucleation for droplets of sufficiently small size  $-5 -10 \mu\text{m}$  depending on the insoluble particle concentration of the water.

These two processes now act sequentially to lead to ice formation. First, as the relative humidity increases in lifting, hygroscopic nuclei grow to haze droplets, with size determined by the RH and the nucleus composition and mass. At 100% RH size equilibrium is reached quickly (equilibrium time  $\approx D r^2/\pi^2$ ) and D is  $5 - 10 \text{ cgs.}$  to give a uniformity time constant of millisecc, which can be neglected. With increase of supersaturation, droplets containing larger masses are activated first to grow as cloud droplets according to the classical Kohler curves - which freeze homogeneously near  $-40^{\circ}\text{C}$  for  $1 \mu\text{m}$  and a little warmer for  $10 \mu\text{m}$ . Inactivated haze droplets by contrast dilute considerably less and only freeze homogeneously at considerably lower temperature. This may be approximated by  $1.86 i m C$  ( $i$  = Van't Hoff factor;  $m$  = molal concentration). With  $m$  as large as 10 and  $i = 3$  (ammonium sulfate) such haze particles may supercool substantially below  $-40^{\circ}\text{C}$ . Ice nucleation and freezing therefore occurs first in the larger particles which grow and dilute first. The evolution of the droplet spectrum and the ice spectrum therefore depends on the vertical velocity and, critically, on the cloud base temperature,  $T_b$ . If  $T_b$  is less than  $-40^{\circ}\text{C}$ , any cloud droplet activated freezes at a small size as  $m$  reduces to an appropriate value. It grows from the vapor and as others freeze, the ambient

supersaturation is limited by the uptake of vapor, so that further activation of the haze droplet is inhibited and the freezing rate drops rapidly. At temperatures somewhat above  $-40^{\circ}\text{C}$ , by contrast, the supersaturation - time profile is controlled by the competitive effects of the activated droplets which limits supersaturation to a few percent at most, and reduction by droplets with insoluble nuclei which freeze and grow from the vapor which remove vapor more effectively than a particle growing as a sphere. At still warmer temperatures with sparse ice crystal concentration, the effect of crystal growth on supersaturation can be neglected.

### 3. The model

The consequence of this is that we need to carry out a careful numerical integration to give the nucleation and growth rate if the ice crystals from measured values of CCN - possibly estimated from CN, - ice crystal nucleation by heterogeneous process - best estimated from measurements of ice directly in the absence of likely secondary ice production processes. The likelihood is that the processes described above will be monotonic with temperature (height) to give a size distribution which gives more crystals at smaller sizes. This leaves vertical velocity near the  $-40^{\circ}\text{C}$  level as a potential variable to give bimodal or more complex size distributions of particles. Thus a dramatically bimodal spectrum can arise from nucleation and growth of a few droplets at low temperature which fall into weak new updraft. A knowledge of these processes is possible from the polycrystallinity of the crystals which subsequently grow from the vapor, with smaller droplets freezing at higher temperatures giving single crystals and larger droplets freezing at lower temperature giving polycrystals as, for example, rosettes of columns or possibly plates.

### 4. Conclusion

The detail of measurements of particularly CCN at these levels is still quite sparse, although CN are somewhat more available. We need quite specific measurements of CCN spectra with respect to the large and small crystal formation at different temperatures near the  $-40^{\circ}\text{C}$  level together with dew point, to give sufficient insight into the physics of cirrus or cloud formation to enable realistic numerical studies to be made along the lines outlined above.

### Acknowledgment

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## NUCLEATION AND CRYSTALLIZATION OF HIGHLY SUPERCOOLED AND SUPERSATURATED STRATOSPHERIC AEROSOL

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The nucleation and growth processes of Polar Stratospheric Clouds (PSC) and the physical chemistry involved in their production is investigated in the laboratory. As hygroscopic aerosols in the atmosphere concentrate, or dilute under changing atmospheric conditions; they may become supersaturated with respect to the solute phase or a hydrate thereof and supercooled with respect to ice. Laboratory studies of bulk samples (0.01 ml) in solution of  $H_2SO_4$ ,  $HNO_3$ ,  $(NH_4)_2SO_4$ ,  $(NH_4)HSO_4$  and NaCl show that both metastabilities can exist in the atmosphere at low temperature. Properties of the solution are inferred by examining phase change induced under imposed uniform conditions; a glass transition may exist. Results are applied to PSC particles and possible chemical reactions at varying concentrations in solution or on particle surfaces.

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