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SECOND SEMI-ANNUAL REPORT

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ABSTRACT

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Since the beginning of NASA Grant NAG-1-627 in January, 1986, four sets of experiments have been conducted.

1. THE EFFECT OF ASPECT RATIO ON NUCLEATION:
Supersaturated solutions were conditioned at different aspect ratios before crystal growth. The conditioned solutions were poured out into dished to initiate crystal nucleation and growth. The rate of growth was measured microscopically and found to depend upon the aspect ratio. Secondly, the number and size of crystals formed was found to depend upon the aspect ratio. The data support the above conclusion, but do not prove it.

2. PRACTICAL CRYSTAL GROWTH:
Advantage was taken of using the aspect ratio and controlling the fluid flow patterns to grow optically clear crystals that are doped with various inorganic ions. The crystals grow rapidly, and they have been sent to NASA-LaRC for analyses. Thirteen crystal systems have been tried, and eight have resulted in suitable crystals.

3. RATE OF DIFFUSION FROM GELS:
Data have been gathered for the examples needed to support a NASA patent application (LAR-13607). Four diffusing systems have been used. It may be necessary to extend the data to additional gels and reagents.

4. FLUID FLOW SCHLIEREN SYSTEM:
The optical system needed to view and to record the fluid flow in crystal growth and in systems that model Bridgman growth of semiconductors has been assembled and is operational. [This has been no mean task given the building renovation and the three moves from one laboratory to another!]

INTRODUCTION:

As crystals grow from solution, there is a removal of solute. The resulting depleted solution is less dense than the original one; and as such the force of gravity causes solutal convection. This convection establishes a flow pattern in the solution from which the crystals grow. The object of the work done during the first part of this grant (NAG-1-627) is to observe this flow and to ascertain its influence on crystal growth.

The work was carried out using an unproven, working hypothesis that precrystalline aggregates exist in solutions.

EXPERIMENT I: EFFECT OF ASPECT RATIO ON NUCLEATION

To ascertain the effect of aspect ratio on crystal growth, a series of experiments were run using identical volumes of the same supersaturated solutions conditioned in test tubes of various aspect ratios. Several supersaturated solutions of ammonium aluminum sulfate (alum) were prepared by dissolving 18.4 to 27.9 grams of the solid in 100.0 milliliters of deionized water. The solution was heated to boiling to eliminate all nuclei, and then exactly 5.00ml of the solution was pipetted into three different size test tubes. The same volumes of liquid in test tubes of various heights resulted in different aspect ratios as indicated in Figure 1. These test tubes were then placed in a constant temperature bath and held at a temperature which is slightly above room temperature for at least eight hours. No crystals nucleated or grew under these conditions. The tops of the test tubes were at room temperature (20° -22°C) while the bottoms of the tubes were held at bath temperature (29.2°C). After conditioning, the tubes were emptied into three-part petri dishes, covered, and allowed to sit at room temperature. Within two hours in most cases crystals developed; but the number of crystals, i.e., the number of nuclei, formed in each case was different. Figure 2 is a sketch of a typical result. Even though the same volume of the same solution held under the same conditions was poured into identical sections of dishes, different numbers of nuclei formed. The experiment was repeated changing the test tubes, dishes, order of emptying, volumes used, and degree of supersaturation. A typical result from a series of runs is summarized in Table 1. Notice that as the degree of saturation decreases, the effect disappears. The aspect ratio is defined to be the ratio of the height divided by the diameter of the solution.

Table 1

Aspect Ratio versus Number and Size of Crystals Formed (Alum preconditioned at 29.2°C)

Conc(g/l)	Aspect Ratio	Number of Nuclei Formed
252	0.66	2 lg + 9 sm
	1.04	9 med
	3.87	765 v sm
227	0.62	3 lg + 2 sm
	1.60	41 med
	3.80	96 sm
204	0.59	105 sm
	1.55	41 sm
	3.60	15 lg
185	0.59&1.5&3.6	no significant difference

In another series of experiments, the rate of crystal growth was measured microscopically as a function of the aspect ratio. The results are summarized in Table 2 and Figure 3. The large statistical variations result in part because measurements were made on several crystal faces of several crystals in each run. Improved results would be obtained if measurements were made on only one type of crystal face for each run.

Table 2

Microscopically Measured Rates of Crystal Growth

Aspect Ratio	Rate of Growth/um s^{-1}
0.7	---(too many nuclei)
1.3	0.464+/-0.088
2.5	0.634+/-0.099
3.6	0.474+/-0.090
4.7	0.466+/-0.055
5.5	0.448+/-0.020

In general, the smaller the aspect ratio the greater will be the growth rate, the larger the crystals, and the fewer the number of nuclei formed. As the degree of supersaturation increases to a maximum or as it decreases to barely over saturation, the effect of aspect ratio disappears. At high supersaturation there is too great a degree of aggregation and thus too great a tendency to form nuclei, while at low supersaturations the equilibrium in solution does not support sufficient aggregation for fluid flow to become significant. At high temperatures the weak intermolecular forces in aggregation are disrupted.

The experiments conducted in this series are not conclusive, and they will have to be repeated enough times to get statistically significant numbers of runs and to vary several more of the experimental parameters. The experiments should also be run on more crystal systems. This series of experiments was temporarily set aside because it is not the main purpose of the project. More time would be needed to gather the statistical data, and there may be simpler ways of proving the existence of precrystalline aggregates.

EXPERIMENT 2: PRACTICAL CRYSTAL GROWTH

The practical application of experiment I was tried. If precrystalline aggregates exist in solution and if solutions can be conditioned prior to crystal growth, perhaps this can be used to improve the rate of growth and the quality of crystals. Consequently, a series of experiments were made with several crystalline substances doped with cations. The crystals grew well and quickly. Table 3 summarizes the types of crystals grown or attempted using these techniques. They have been sent to NASA-LaRC for optical analyses.

Table 3

<u>Crystals Grown</u>

Alum (---)
Alum (Cr^{3+})
Alum (Fe^{3+})
Alum (Co^{2+})
Alum (Ni^{2+})
Alum (Cu^{2+})
KHP (---)
KHP (Co^{2+})

<u>Crystals Attempted</u>

KHP (Ni^{2+})
KHP (Cu^{2+})
Salicylic Acid (dye #5)
Potassium Citrate (---)
TGS (---)

The following general observations can be made about the crystals grown:

1. Precrystallization conditioning reduces nucleation and increases the rate of growth. These crystals can grow up to eight to twelve grams in 24 to 48 hours.

2. Modifying the flow which occurs as a result of crystal growth increases the clarity of the resulting crystals.

3. Crystals grow in a "parent-child" relationship. That is, one crystal begins to grow first, and this sets up a dominant fluid flow pattern as shown in Figure 4. Nearby another seed spontaneously begins to grow in the shadow of this flow pattern. This "child" usually grows with far fewer crystal defects and is far clearer than the "parent" one. It grows to almost the same size as the parent.

4. Because of the fluid flow field, as the "parent" crystal reaches a "mature" size the flow is no longer uniform over the top face. This results in a conical pattern of defects. These defects can be seen as a cloudy pattern in the crystal. Further, within the cone of defects a "kernal" develops that is very clear. This "kernal" can be cut out and polished. This too has been sent for analyses.

EXPERIMENT 3: RATE OF DIFFUSION FROM GELS

In the early part of the summer, while the renovation move was just beginning, we ran a series of experiments to gather the data required for examples in a NASA patent application for the use of gels to safely deliver chemicals in experiments conducted in space. (LAR-13607). Several gels were prepared doped with sodium chloride, potassium chloride, potassium bromide, or cobalt chloride. These were prepared in straws and exuded into distilled water at the beginning of the measurement. The rate of diffusion of the added chemicals out of the gels were determined and a typical result for sodium ion is illustrated in Figure 5.

EXPERIMENT 4: FLUID FLOW SCHLIEREN SYSTEM

To observe the actual fluid flow that accompanies crystal growth, an optical bench with Schlieren Optics has been set up. The data can be recorded on video tape as well as photographically. This will now be used to record the fluid flows accompanying crystal growth and to test transparent fluids that will model the conditions occurring in Bridgman crystal growth.

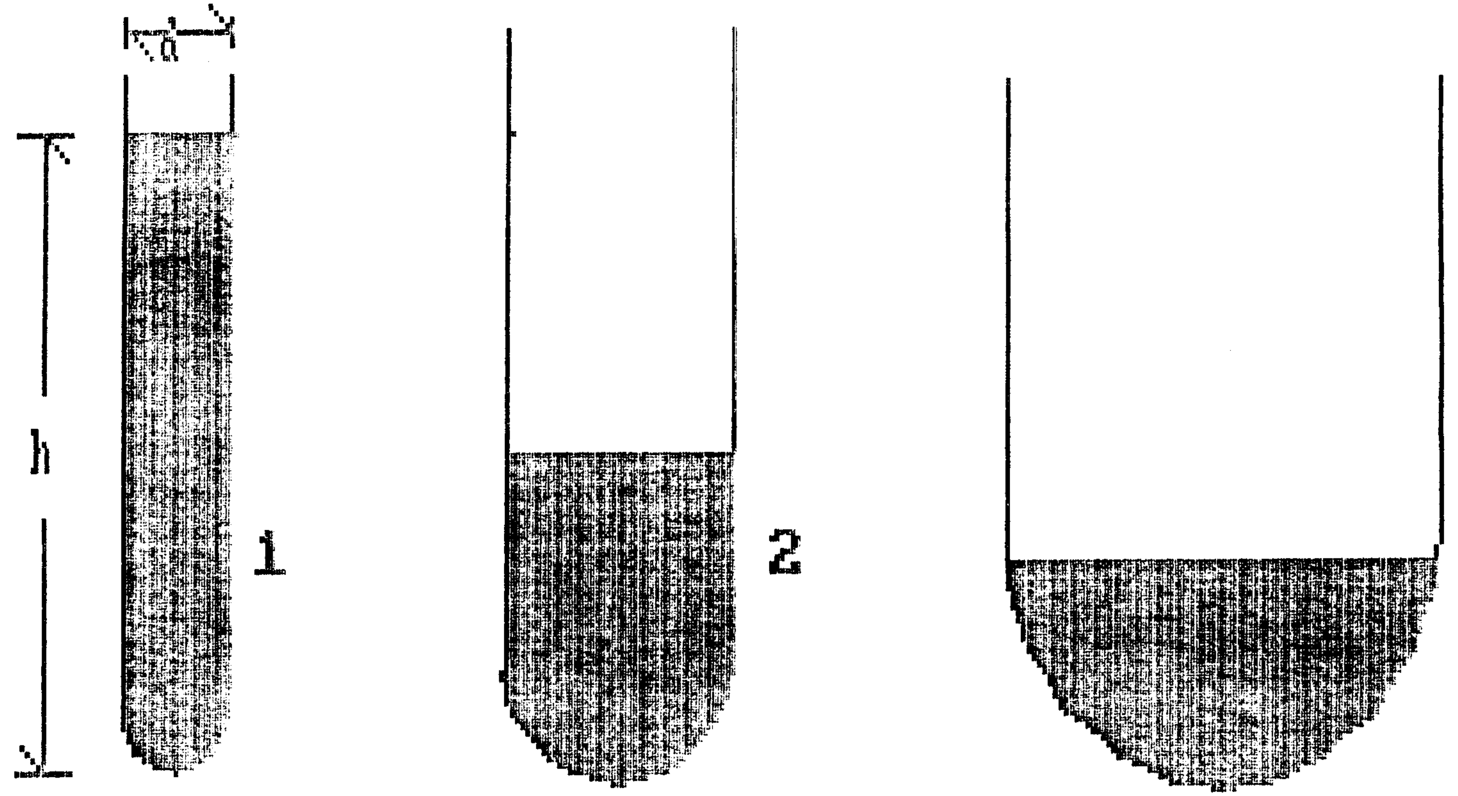

FIGURE 1

Same volumes at different aspect ratios

$R_{as} = h/d$, $R_{as}(1) > R_{as}(2) > R_{as}(3)$

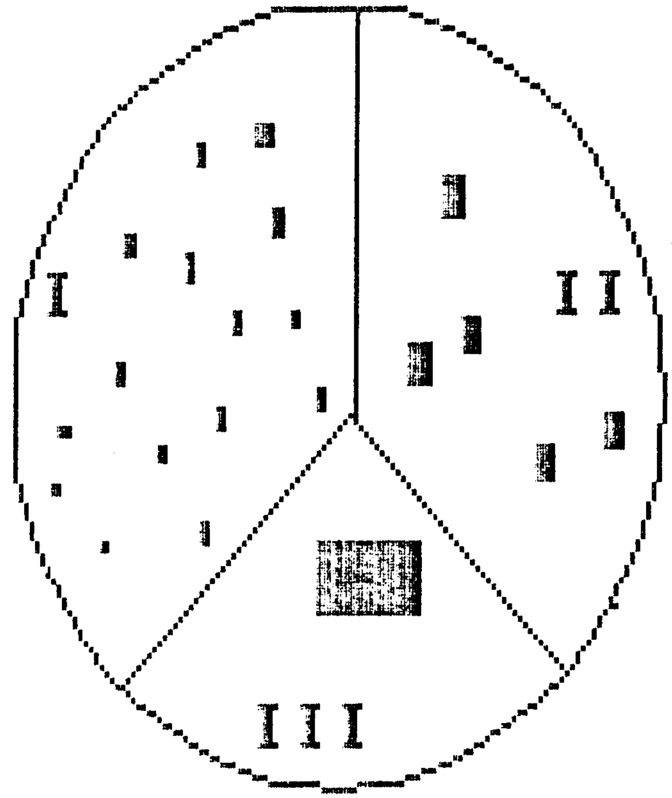

FIGURE 2

Aspect ratios affect number of nuclei.

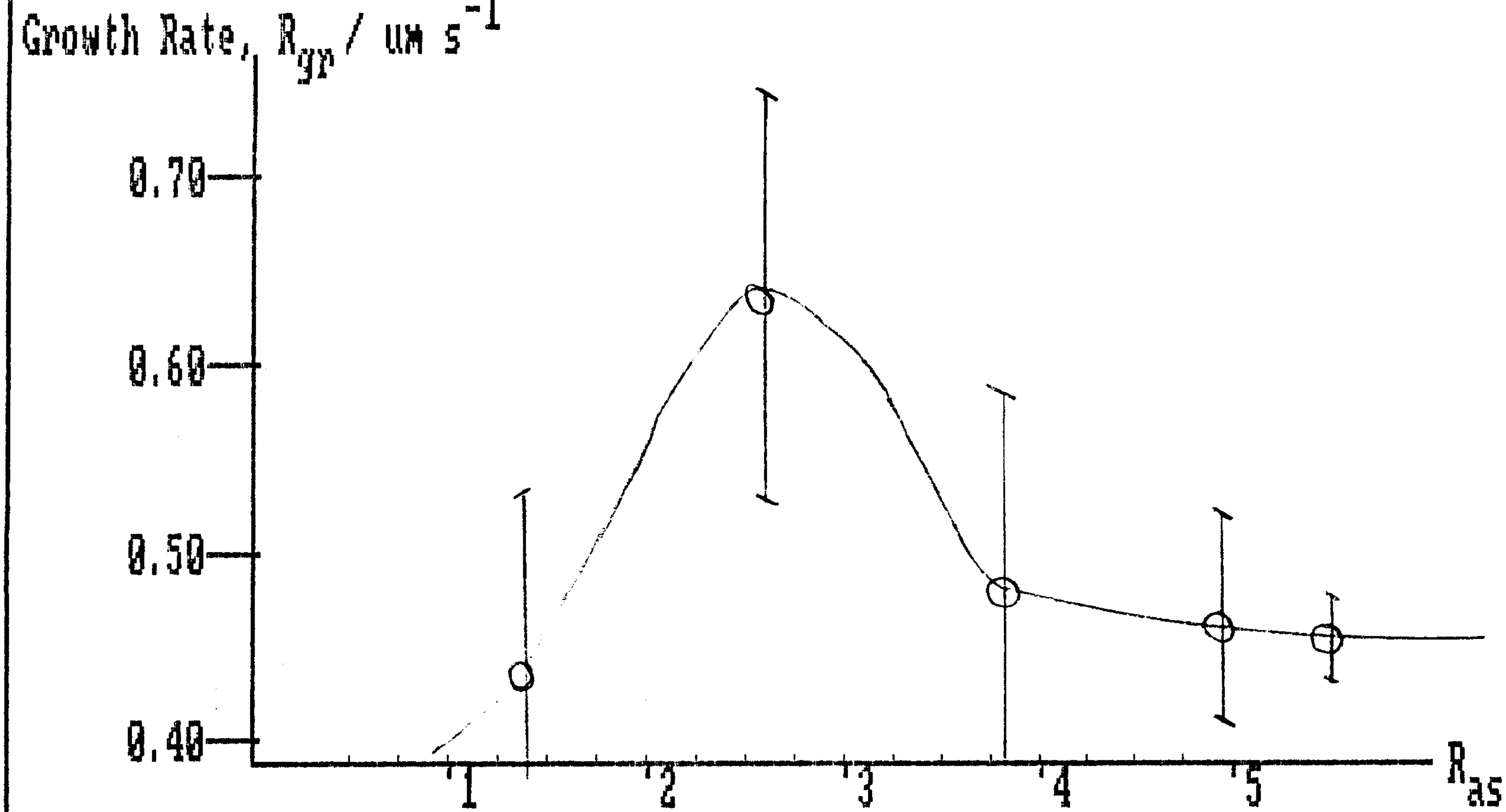

FIGURE 3

Rate of Growth vs. Aspect Ratio

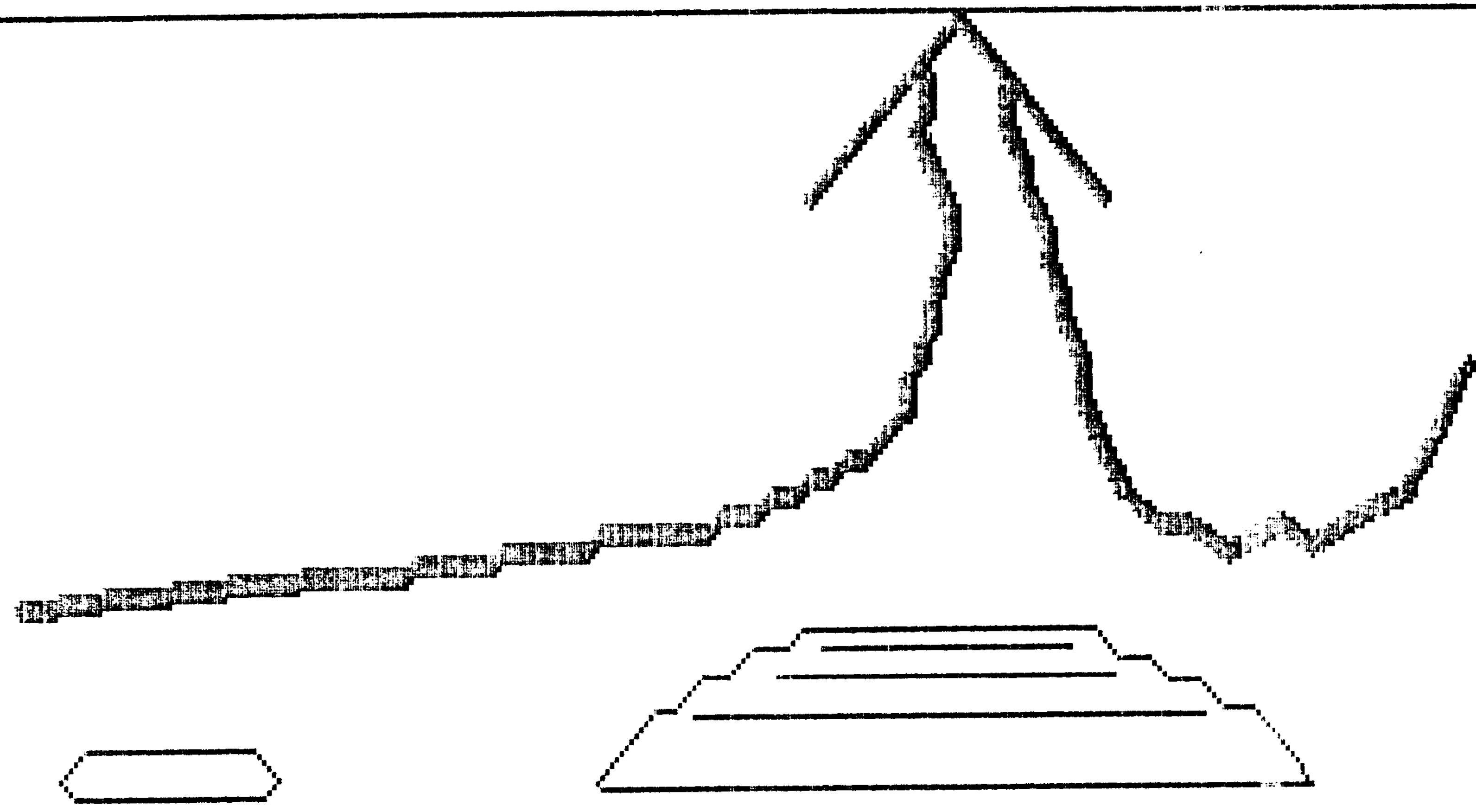

FIGURE 4

Fluid Flow Pattern and Crystalline "Parent-Child"

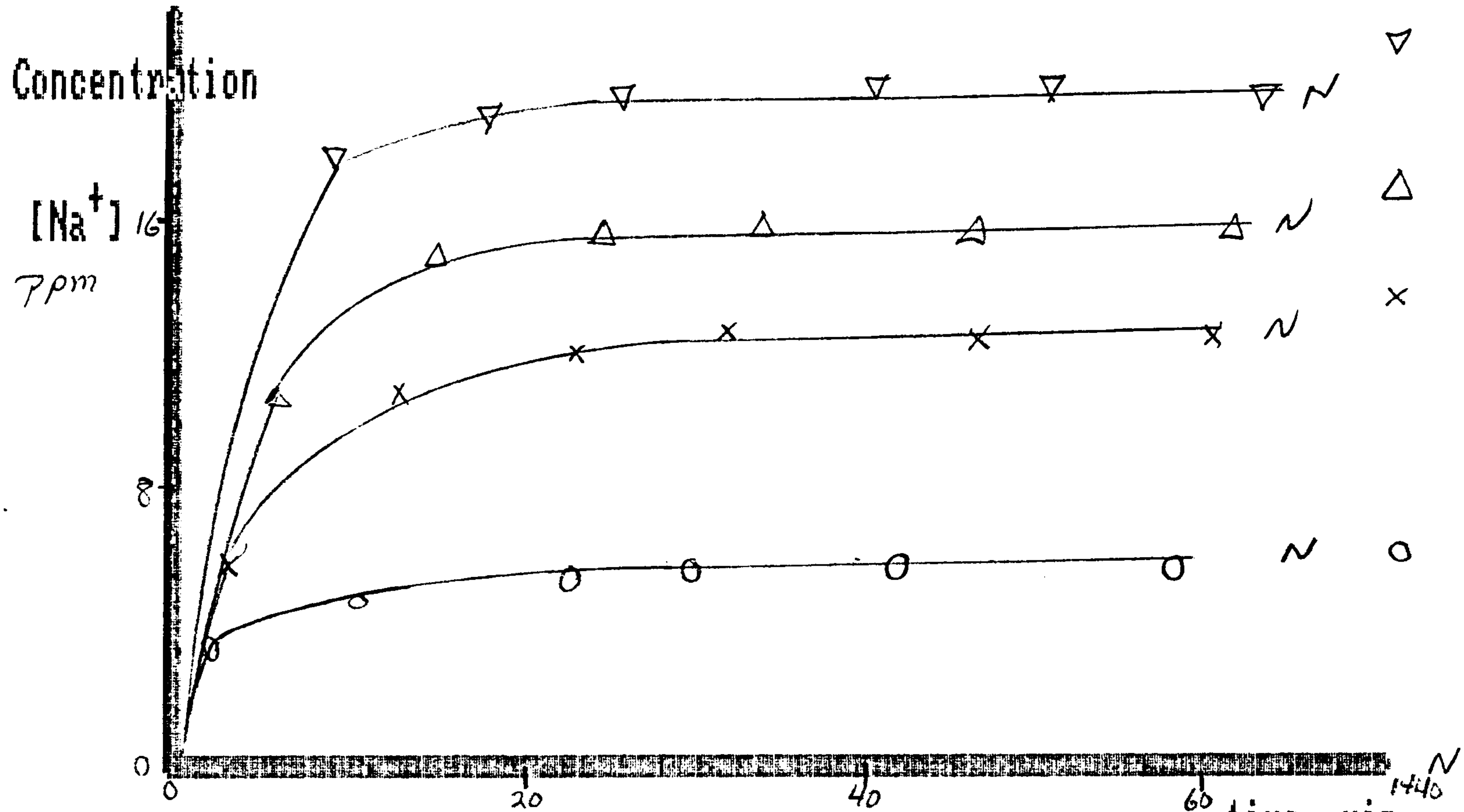

FIGURE 5

Rate of Delivery of Sodium Ions from a Gel into Solution