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THE GROWTH RATE OF ICE CRYSTALS:
THE PROPERTIES OF CARBON DIOXIDE HYDRATE
A REVIEW OF PROPERTIES OF 51 GAS HYDRATES

United States Department of the Interior



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By John G. Vlahakis; Hsiao-Sheng Chen;
Mohamad S. Suwandi; Allen J. Barduhn,
Syracuse University, Syracuse, New York, for
Office of Saline Water, J. W. O'Meara,
Director; W. Sherman Gillam, Assistant
Director, Research; Sidney Johnson, Chief,
Applied Science Division

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FOREWORD

This is one of a continuing series of reports designed to present accounts of progress in saline water conversion and the economics of its application. Such data are expected to contribute to the long-range development of economical processes applicable to low-cost demineralization of sea and other saline water.

Except for minor editing, the data herein are as contained in a report submitted by the contractor. The data and conclusions given in the report are essentially those of the contractor and are not necessarily endorsed by the Department of the Interior.

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ABSTRACT

This is Report No. H-13 from the Hydrate Project of the Department of Chemical Engineering and Materials Science at Syracuse University, and it consists of 4 parts. They cover work done mainly during the year ending June 30, 1972, but the research on ice crystal growth extends back farther in time.

Each part of this report is separate from the others and has its own numbering system for tables, figures, and literature cited. The laboratory work was done by the student whose name appears in the heading. Mr. Chen's work was done as part of requirement for an M.S. in Chemical Engineering, and Mr. Vlahakis' work was for his Ph.D. in Chemical Engineering. Mr. Suwandi's work was a special project done in the Spring of 1972.

A brief review is given of the status of choosing a hydrating agent for use in the hydrate process for desalting. Nine agents are listed as not yet having been eliminated from consideration, and, of these, at least 4 appear to be good possibilities: R-12(CCl_2F_2), R-142b(CH_3CClF_2), R-152a(CH_3CHF_2) and R-31(CH_2ClF). Of these, R-31 now looks best, but economic analysis and further laboratory work are required before more firm decisions can be made.

Part 2 covers our work on CO_2 hydrate for which the basic information are now available to make pilot plant designs and economic analyses. Pressure-temperature-concentration data for the system CO_2 -NaCl- H_2O in the hydrate forming region for temperatures from -10°C to $+10^\circ\text{C}$, pressures from 10 to 50 atm. and concentrations from 0 to 10 weight percentage of NaCl, were accurately measured. In addition, the CO_2 hydrate eutectic temperature with NaCl and the P-T relation for the equilibrium among $\text{NaCl}\cdot 2\text{H}_2\text{O}(\text{solid})$, CO_2 Hydrate(solid), saturated aqueous solution, and gas have been determined. In the latter case, temperatures ranged down to -14°C . The equilibria with NaCl present have not been measured previously and are useful for designing a CO_2 hydrate process for desalting sea water and for the hydrate eutectic process for separating saline waters into water and solid salt, leaving no brine product.

From the basic experimental data taken, the composition of carbon dioxide hydrate was calculated to be 7.30 ± 0.13 moles H_2O /mole CO_2 by using Miller-Strong's method. Also, the heats of formation and the invariant points of the hydrate were found to be:

<u>Invariant Points</u>	<u>Temperature($^\circ\text{C}$)</u>	<u>Pressure(atm)</u>	<u>$-\Delta\text{H}^\circ(\text{kcal/g-mole})$</u>
1. With ice, gas, water and CO_2 hydrate(solid)	- 1.48	10.28	14.247
2. With gas, water, CO_2 liquid and CO_2 hydrate (solid)	10.00	44.40	13.886
3. With CO_2 (gas and liquid) Aqueous NaCl solution CO_2 hydrate(solid) $\text{NaCl}\cdot 2\text{H}_2\text{O}(\text{solid})$	- 9.6	26.47	-- (24.2% NaCl)

Finally, a set of P-T-C data were tabulated for practical application.

Part 3 is a review of the known properties of 51 gas hydrates including an extensive table of data and 80 references.

Part 4 is based on the Ph.D. thesis of John G. Vlahakis on ice crystal growth. The linear growth rate in the basal plane of unconfined ice crystals

has been measured in flowing subcooled water and aqueous NaCl solutions. Growth rates were measured at five NaCl concentrations: 0.15 to 6.0 wt.%. At each NaCl concentration at least three solution velocities were employed: 0.20, 0.85, and 3.9 cm/sec. In distilled water five different flow velocities were investigated in the range 0.042 to 1.0 cm/sec. For all cases, both pure and salt water, subcoolings ranged from 0.05 to 0.9°C.

The distilled water work at low flow velocities has shown that Fernandez' equation still holds down to the lowest solution velocity studied, $V = 0.042$ cm/sec, for subcoolings less than 1°C. The growth rate of ice is then proportional to the $1/2$ power of the water velocity and the $3/2$ power of the subcooling. The growth rate model of Fernandez assumes that the factor completely controlling dendritic ice growth is the rate at which the latent heat of solidification is transferred by convection from the crystal to the flowing water. By using our experimental growth rate equation a value for the ice-water interfacial tension, γ , was derived. Our value of 33 ergs/cm² compares well with a value recently reported in the literature.

In salt solutions, however, Fernandez' equation does not hold well. Instead of a monotonically decreasing growth rate with increasing salt concentration for all subcoolings and solution velocities, a growth enhancement effect has been observed which is greatest at the largest subcooling and the lowest solution velocity studied ($V = 0.20$ cm/sec). The greatest observed growth rate enhancement over that in pure water is about 100% at $\Delta T = 0.7^\circ\text{C}$ and 0.5% NaCl. The anomaly tends to disappear at the highest solution velocity studied ($V = 3.9$ cm/sec).

In the equation for the temperature dependence of ice growth, $v = a T^n$, n approaches $3/2$ as the solution velocity increases to $V = 3.9$ cm/sec. At $V = 0.20$ cm/sec, n is near 2 for all but the lowest solution concentration (0.15% NaCl).

The solute anomaly was also demonstrated for 1.5% glucose solution showing that this effect is not confined to electrolytes.

Radii of curvature of the ice crystal tips were measured as a function of subcooling both in distilled water and in 0.15% NaCl solution. The data in distilled water show an inverse relation to subcooling but are 6.5 times larger than that predicted by Fernandez. The data in 0.15% NaCl solution have a steeper negative slope and are of the same magnitude as that in distilled water.

CHOOSING A HYDRATE FOR DESALTING

Choosing a hydrating agent for use in the hydrate process to desalt saline water is a difficult problem because the economic analysis needed to make such a choice depends on a rather large number of properties of the agent and its hydrate. For the agent, these properties include its cost, flammability, solubility in water and salt solutions, toxicity, corrosivity, rate of hydrolysis and vapor pressure. For the hydrate, the important factors are the temperature and pressure of formation, its composition, its density, its heat of formation, the size, shape, and permeability of the crystals formed in a continuous reactor, and the rate at which hydrate forms under various conditions. It is probable that the temperature at which the raw saline water is available will also affect the choice of agent, with the favor weighted toward the higher temperature hydrates when the feed water temperature is high.

The information needed for the economic analysis is thus very extensive and is almost never available in the literature. The program conducted at Syracuse University has had as one of its goals the determination of those properties needed for design and economic evaluation of the various agents. Any one unknown property may completely eliminate an agent from serious consideration and it is unfortunate that there is no certain way for a priori detection of this critical property. If there were, then this property could be determined first and if the agent were thus eliminated, no further work would need be done. In the case of methyl bromide hydrate we did a lot of work on its thermodynamics and kinetics of formation and later found out that its rate of hydrolysis was so high, that regardless of the excellence of its other properties, it was definitely eliminated from further consideration. In another example, the Sweetwater Development Company went clear up to the stage of constructing and operating a 10,000 gal/day propane hydrate pilot plant and then found out that propane hydrate crystals were just too small and dendritic to form beds which could be washed economically. The beds were extremely compressible and had a permeability on the order of 10^{-8} cm². It took much time, effort, and money to discover that propane does not form a hydrate that is suitable for use in a desalting process.

Agents which have not yet been eliminated as potentially useful for desalination are listed below in order of increasing critical decomposition temperature.

TABLE I
HYDRATES POTENTIALLY USEFUL FOR
DESALINATION AS OF 1972

Agent	Critical Decomposition Conditions		
	Temperature	Abs.	Gage
R-21(CHCl_2F)	8.7°C	760 mm	0 psig
Carbon Dioxide	10.0	33,740	638
R-12(CCl_2F_2)	12.1	3,435	52
R-142b(CH_3CClF_2)	13.1	1,743	19
R-152a(CH_3CHF_2)	14.9	3,270	49
Cyclopropane	17.0	4,470	72
R-31(CH_2ClF)	17.9	2,147	27
Methyl Chloride	20.4	3,640	56
Chlorine	28.3	6,390	109

Three of the above agents form at moderate pressures (0 to 27 psig) and these are: R-21, R-142b, and R-31. Sufficient data are available on all of these to make a preliminary economic analysis of their suitability for commercial use. Only an engineering staff in a chemical plant or plant construction company can make a useful analysis. Such a study must be made where plant operating talent, engineering skill, economic knowledge and general process development experience are all simultaneously available. Cost estimates made in universities or even in commercial establishments where one of the above requirements is missing are normally of dubious value. Even under the best conditions, however, the cost analysis made from basic laboratory data alone should be considered tentative since pilot plant work on a larger scale is needed before any capital can be ventured for larger scale development or plant construction. In any event, the three low pressure hydrates have no known drawbacks and warrant serious consideration for use in desalting. Of these, the R-31 looks best because of its high formation temperature, its compact chunky crystals and the permeable beds they form.

The five medium pressure hydrating agents (49 to 109 psig) are: R-12, R-152a, cyclopropane, methyl chloride and chlorine. Methyl chloride hydrolyses at an acceptable rate with no metals present, but it is not known what catalytic effect the metals may have. Otherwise, there are no known defects to these for use in desalination. R-12 has already been tried by Koppers Company in their 10,000 gal/day hydrate pilot plant at Wrightsville Beach, but the results were indecisive and the work was stopped for reasons irrelevant to process economics. Cyclopropane hydrate forms at a reasonably high temperature (17°C) and fairly high pressure, but nothing else is known about it except that it probably does not hydrolyse at all. If its crystals form as do those of

propane it would be unsuitable, but there is no evidence of this. Chlorine hydrate forms at the highest temperature of all known hydrates (28.3°C) but at the fairly high pressure of 109 psig. Its advantages are the very low cost of chlorine (3¢/lb) and the high formation temperature. Its obvious disadvantages are its strong corrosivity in water solution, the difficulty of stripping it from water below about 100 ppm, and its higher formation pressure.

The relative effect on cost of water produced by operating temperature vs operating pressure are not known, so we cannot answer here the question of the disadvantage of operating at 50 psig vs say 20 psig, or the advantage of operating at 20°C vs 10°C. There is no doubt that higher operating temperatures are qualitatively a big advantage, but it is the quantitative estimate of this that is lacking. Some of the advantages of high temperature hydrates have been looked at quantitatively (Briggs).

The remaining hydrate of carbon dioxide has the disadvantage of forming at relatively high pressure (640 psig). It has the advantage, however, of being non-corrosive, very cheap and easily available. The fluorinated hydrocarbons cost from 25¢ a lb. up. Data for preliminary design and economic studies are incomplete and, in the next section, we describe results of our work on the thermodynamics of carbon dioxide hydrate. The presumption regarding high pressure hydrates is, of course, that the cost of vessels designed for such pressures would be high and thus the process would be uneconomical. It is germane then to ask the questions (a) how much more does it cost to operate at high pressure?, and (b) is this compensated for by the other properties of the hydrate? It is only the final economic analysis using all the properties of the system that tells us that hydrate "x" is better than hydrate "y".

In addition to the new work on carbon dioxide hydrate presented later, we have made an extensive tabulation of all the common properties of all known gas hydrates which brings together in one place the considerable number of data taken at Syracuse along with the data of others going back to the nineteenth century.

The last section of this report covers 3 years work on the growth rate of ice crystals in flowing subcooled water and salt solutions. A small fraction of this work was reported in 1969 in OSW R and D Report No. 497, but that part is included in the larger compilation here.

THE PROPERTIES OF CARBON DIOXIDE HYDRATE

(H.-S. Chen)

I. LITERATURE SURVEY

Prior work in the investigation of the properties of carbon dioxide hydrate can be divided into two parts: the determination of the hydrate composition and the phase diagram of this hydrate.

The composition of the hydrate has been investigated by many workers from the time of Wroblewski (R-38,39) in 1882. Most of the composition data were determined from direct analysis and only a few of them were obtained by using thermodynamic methods or X-ray analysis. This is the reason why the previous data covered the very wide range from $\text{CO}_2 \cdot 5\text{-}3/4 \text{ H}_2\text{O}$ to $\text{CO}_2 \cdot 9\text{H}_2\text{O}$. Probably there is a precise value at any one temperature. This value may vary with temperature, but within the narrow range from -1.5 to 10°C its change may be quite small. In this thesis, a single value is reported for this range.

The decomposition pressure of the carbon dioxide hydrate was also reported by numerous investigators since Wroblewski. The phase diagram for the $\text{CO}_2\text{-H}_2\text{O}$ -hydrate system from -16°C to 10°C was completed by Larson (R-15) in 1955, but the data on the carbon dioxide-NaCl aqueous solution were not available until now. These data are necessary for design of the hydrate process to separate fresh water from saline water.

In this work, the decomposition pressures of carbon dioxide hydrate in NaCl aqueous solution of different concentrations were accurately measured. The composition of the hydrate was calculated from these data by using Miller-Strong's method (R-17,18). The standard heat of formation of the hydrate was also calculated from the equilibrium data of $\text{CO}_2\text{-H}_2\text{O}$ -hydrate system by using Pierson's method (R-22). The pressure-temperature-concentration data for carbon dioxide hydrate in NaCl solutions were then tabulated for engineering use.

The hydrate of carbon dioxide was first discovered by Wroblewski who also measured the decomposition pressure of the hydrate between 0°C and 6.8°C in 1882. He also reported that the composition of the hydrate determined by direct analysis was $\text{CO}_2 \cdot 8\text{H}_2\text{O}$. Later in 1897 Villard (R-35) extended Wroblewski's work and published the decomposition pressure-temperature curve from -6°C up to 10°C . He also analyzed the hydrate directly and reported its composition as $\text{CO}_2 \cdot 6\text{H}_2\text{O}$. Due to the great difference in the measurement of Wroblewski's and Villard's work, Hempel and Seidel (R-12) decided to measure it again. They reported the value as $\text{CO}_2 \cdot 8\text{H}_2\text{O}$ and $\text{CO}_2 \cdot 9\text{H}_2\text{O}$, but they didn't mention which one was more accurate. The method they used was direct analysis.

In 1902 de Forcrand (R-8,9) computed the composition of the hydrate by using the thermodynamic method (see Chapter III-B-1). His result was $\text{CO}_2 \cdot 6\text{H}_2\text{O}$. Later, Bouzat and Azinieres (R-4) studied the hydrate and assumed that carbon dioxide hydrate was similar to chlorine hydrate, $\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, because these two hydrates were alike with respect to their other properties.

In 1925 Tammann and Krige (R-32) measured the decomposition pressure of the hydrate between -20°C and -43°C , but their pressures were too low to be credible. The reason explained by Larson was that the formation of an ice layer over the surface of the hydrate crystal to such an extent that no further decomposition of the hydrate was possible, i.e., the system was not in equilibrium.

Herreillers (R-13) studied carbon dioxide hydrate in 1936. His thesis could not be obtained, but some of his results were reported by other workers (R-2,19,29). He gave 14.4 kcal/g-mole for the heat of formation of the hydrate and 10.2°C for the critical decomposition temperature.

In 1946 Frost and Deaton (R-10) reported the decomposition pressure of the hydrate between 0° and 10°C. They also determined the composition of the hydrate, by direct analysis, to be $\text{CO}_2 \cdot 7\text{H}_2\text{O}$. Katz and Unruh (R-33) studied the gas hydrate of carbon dioxide and methane mixture, and measured the decomposition pressure of carbon dioxide hydrate from 4.06°C to 9.89°C. In their report the critical point was 9.89°C and 44.42 atm. This temperature is somewhat lower than the other workers' value.

In 1951 Claussen (R-6,7), Stackelberg and Müller (R-27,28) studied the structure of water molecules in CO_2 hydrate crystals by using X-rays. They suggested that the structure of the hydrate is a unit cell consisting of forty-six water molecules enclosing two small holes and six larger ones into which CO_2 molecules can pack. With CO_2 molecules filling all holes, the composition of CO_2 hydrate is $\text{CO}_2 \cdot 5\text{-}3/4 \text{H}_2\text{O}$. Usually, the hydrating number will be greater than 5.75 because it's not often that all holes are filled.

Larson (R-15) worked out the phase diagram of the carbon dioxide-water system in 1955. He sketched three equilibrium curves with temperature ranging from -16°C to 12°C. These curves were (a) the equilibrium between gaseous carbon dioxide, liquid carbon dioxide and hydrate; (b) the equilibrium between gaseous carbon dioxide, hydrate and aqueous solution; (c) the equilibrium between gaseous carbon dioxide, hydrate and ice. He also measured the equilibrium pressure between hydrate, gaseous carbon dioxide and NaCl aqueous solutions with initial concentration 1N, but he didn't measure the concentration of the solution at equilibrium, which makes the data of little use. He determined the composition of the hydrate to be $\text{CO}_2 \cdot 6.07 \text{H}_2\text{O}$ by using de Forcrand's method (R-8), and also calculated the standard heat of formation of carbon dioxide hydrate to be 14.4, 15.8 and 16.3 Kcal/g-mole at temperature -1.5°C, 3.9°C and 8.5°C, respectively.

Recently, Takenouchi and Kennedy (R-31) studied the phase diagram of carbon dioxide hydrate in the condensed region at high pressures and at temperatures above 10°C up to 19.5°C. The equilibrium curve they determined was for the equilibrium between liquid carbon dioxide, solution and hydrate. They also calculated the density of the carbon dioxide hydrate crystals to be 1.15 g/cm³ by using the Clausius-Clapeyron equation.

The decomposition pressure of carbon dioxide hydrate was recently measured by Miller and Symthe (R-19) at temperatures ranging from -121°C to -81°C. There are no data on the decomposition pressure of carbon dioxide hydrate in equilibrium with gaseous carbon dioxide and NaCl aqueous solution.

The compositions of the hydrate determined by various workers and the method they used are listed in Table 1. As we can see from this table, the composition of the carbon dioxide hydrate is still uncertain. The most frequently reported value is around six molecules of hydration.

The work reported below and performed at Syracuse gives rather different values for the heat of formation, the composition and the crystal density of CO_2 hydrate and these new data are presumed more reliable than any heretofore reported.

II. THERMODYNAMICS OF CO₂ HYDRATE

A. Theory for the Heat of Hydrate Formation (R-1,22)

For the system CO₂-H₂O with three phases present, from the phase rule, there is only one degree of freedom and the pressure is a function of temperature. The Clausius-Clapeyron equation can be written as:

$$T \frac{dP}{dT} = \frac{\Delta H_a}{\Delta V_a} \quad (1)$$

where

ΔV_a = actual volume change in the reaction under equilibrium condition

ΔH_a = actual enthalpy change in the reaction under equilibrium condition for the same quantity of substance

Define an arbitrary heat quantity Q

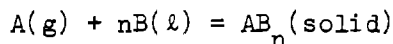
$$Q = R \frac{d \ln P}{d(1/T)} \quad (2)$$

If the experimental data are plotted in the form $\ln P$ vs $1/T$, one can calculate Q from the slope of the resulting lines.

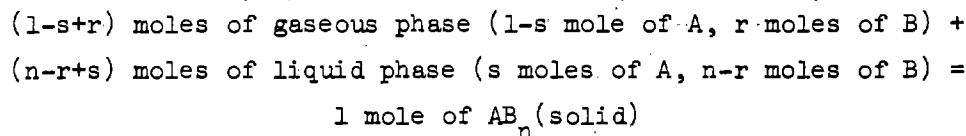
Combining Equation (1) and Equation (2),

$$\Delta H_a = - \Delta V_a \cdot (P/RT) \cdot Q \quad (3)$$

Now, considering the three phase equilibrium



Because of the volatility of B, some of it occurs in the vapor phase and also because of the solubility of A in B, some of it occurs in the liquid phase. Thus, during the decomposition of one mole of AB_n , s moles of A remain in the liquid phase while 1-s moles of A go into gaseous phase. At the same time, r moles of B vaporize while n-r moles of B stay in the liquid. The reaction can thus be rewritten as follows:



The mole fraction of A and B in each phase can be expressed as:

$$\begin{aligned} y_B &= \frac{r}{1+r-s} & y_A &= \frac{1-s}{1+r-s} \\ x_B &= \frac{n-r}{n-r+s} & x_A &= \frac{s}{n-r+s} \end{aligned}$$

Now, s and r can be calculated from the above equations:

$$r = \frac{1-(n-1)x_A}{1-x_A-y_B} \cdot y_B \quad \text{and} \quad s = \frac{n-(n+1)y_B}{1-x_A-y_B} \cdot x_A \quad (4)$$

ΔH_a and ΔV_a for this reaction are given by:

$$\Delta H_a = h_{AB_n} - (1-s)\bar{h}_{A,G} - r\bar{h}_{B,G} - s\bar{h}_{A,L} - (n-r)\bar{h}_{B,L} \quad (5)$$

$$\Delta V_a = v_{AB_n} - (1-s)\bar{v}_{A,G} - r\bar{v}_{B,G} - s\bar{v}_{A,L} - (n-r)\bar{v}_{B,L} \quad (6)$$

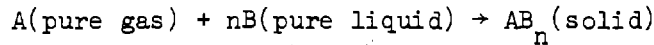
ΔV can also be expressed in molar volume of the gaseous phase and liquid phase, i.e. V_G and V_L :

$$\Delta V_a = v_{AB_n} - (1-s+r)V_G - (n-r+s)V_L \quad (7)$$

By substituting Equation (7) into Equation (3), ΔH_a can be calculated from the following:

$$\Delta H_a = - \left[v_{AB_n} - (1-s+r)V_G - (n-r+s)V_L \right] \cdot (P/RT) \cdot Q \quad (8)$$

ΔH° , the standard heat of formation of AB_n , is defined as the enthalpy change in the formation of one mole of AB_n from pure liquid B and pure gaseous A as an ideal gas at 1 atm. The reaction is as follows:



$$\Delta H^\circ = h_{AB_n} - h^\circ_{A,G} - nh_{B,L} \quad (9)$$

Subtract Equation (5) from Equation (9),

$$\Delta H^\circ - \Delta H_a = (\bar{h}_{A,G} - h^\circ_{A,G}) + n(\bar{h}_{B,L} - h_{B,L}) + r(\bar{h}_{B,G} - \bar{h}_{B,L}) - s(\bar{h}_{A,G} - \bar{h}_{A,L}) \quad (10)$$

For the CO_2 - CO_2 hydrate- H_2O system at temperature from -5°C to 10°C , the pressure of the system is usually above 10 atm. The vapor pressure of pure water at 10°C is 9.2 mm Hg. Compared with the system pressure, the partial pressure of water in the gaseous phase is negligible, and the gaseous phase can be regarded as pure carbon dioxide. Then

$$y_B = 0$$

$$V_G = v_{\text{CO}_2}$$

From Equation (4),

$$r=0 \quad \text{and} \quad s = \frac{nx_A}{1-x_A} \quad (11)$$

Equations (8) and (10) reduce to:

$$\Delta H_a = - \left[V_{AB_n} - (1-s)V_{A,G} - (n+s)V_L \right] \cdot P/RT \cdot Q \quad (12)$$

$$\Delta H^\circ = \Delta H_a + (h_{A,G} - h^\circ_{A,G}) + n(\bar{h}_{B,L} - h_{B,L}) - s(h_{A,G} - \bar{h}_{A,L}) \quad (13)$$

The third and fourth terms of the right-hand side of Equation (13) are the heat of mixing of n moles of B with s moles of A. If the s is very small compared with n , it can be regarded as s moles of A dissolving in an infinite amount of B. The last two terms of Equation (13) can thus be rewritten as $s \cdot \Delta H_{\text{soln}}$. The heat of solution of carbon dioxide in water is taken to be -4.755 Kcal/g-mole (R-15).

The term $(h_{A,G} - h^\circ_{A,G})$ is the compression enthalpy of non-ideal gas. At low pressure this term is usually negligible, but for this work the pressure is 45 atm at the highest and this term should not be neglected. From thermodynamics, the enthalpy change with respect to pressure at constant temperature is,

$$\left(\frac{\partial h}{\partial P} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P \quad (14)$$

The enthalpy change of a fluid relative to its ideal gas state when both are at the same temperature, can be obtained by integrating Equation (14)

$$h_{A,G} - h^\circ_{A,G} = \int_0^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \quad (15)$$

Define the heat of compression as ΔH_{comp} ,

$$\Delta H_{\text{comp}} = h_{A,G} - h^\circ_{A,G} = \int_0^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \quad (16)$$

ΔH_{comp} can be calculated from the above equation provided that the equation of state of the gas is known.

Equation (13) can be rewritten as,

$$\Delta H^\circ = \Delta H_a + \Delta H_{\text{comp}} + s \cdot \Delta H_{\text{soln}} \quad (17)$$

B. Theory for Determining the Hydrate Composition (R-1)

1. de Forcrand's Method (R-8,9)

de Forcrand's method for determining the composition of the hydrate is to use the following relation:

$$n = \frac{\Delta H_2^\circ - \Delta H_1^\circ}{\Delta H_{\text{fusion}}} \quad (18)$$

where

n : the number of water molecules in a hydrate molecule

ΔH_1° : the standard heat of reaction for the following reaction: $A(g) + nH_2O(l) \rightarrow A \cdot nH_2O(s)$ (I)

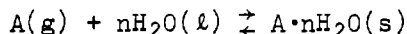
ΔH_2° : the standard heat of reaction for the following reaction: $A(g) + nH_2O(s) \rightarrow A \cdot nH_2O(s)$ (II)

ΔH_{fusion} : the heat of fusion of ice. Usually ΔH_{fusion} is taken to be 1437 cal/g-mole

Both reactions (I) and (II) are taken at the same temperature. ΔH_1° and ΔH_2° can be calculated according to the method discussed in Chapter III-A. There are two defects in using this method. The first one is that many experimental data have to be taken, but only the composition of hydrate at the invariant point with ice, i.e. the lower critical point, can be determined since this is the only temperature at which both reactions I and II can occur at equilibrium. The second one is that we cannot check the result by doing more experiments and taking more data. The more data taken, the greater the probability of accuracy, but there is no way to observe the consistency of the result since only a single value of ΔH results.

2. Miller-Strong's Method (R-17,18)

Miller and Strong considered the equilibrium



in pure water and salt solution. If the equilibrium temperature is the same, the equilibrium constant K is constant.

$$\frac{1}{K} = \frac{\left[a_{H_2O} \right]^n \left[a_A \right]}{\left[a_{A \cdot nH_2O} \right]} \quad \text{pure water} \quad (1) = \frac{\left[a_{H_2O} \right]^n \left[a_A \right]}{\left[a_{A \cdot nH_2O} \right]} \quad \text{in salt solution} \quad (2) \quad (19)$$

The activity of the hydrating agent can be expressed as fugacity. The activity of the solid hydrate is constant at a given temperature. Equation (19) can then be rewritten as,

$$a_1^n f_1 = a_2^n f_2 \quad (20)$$

solving for n

$$n = \frac{\ln(f_2/f_1)}{\ln(a_1/a_2)} \quad (21)$$

where

f_1 = the fugacity of the hydrating agent at T° in the pure water-hydrate system

f_2 = the fugacity of the hydrating agent at T° in the NaCl aqueous solution-hydrate system

a_1 = the activity of water at T° in the pure water-hydrate system

a_2 = the activity of water at T° in the NaCl aqueous solution-hydrate system

The solubility of carbon dioxide in pure water is rather high and its effect on the activity of the water cannot be neglected. Since the solubility of CO_2 in pure water will not exceed 3 mole percent within the hydrate range, it may be suitable to assume that Raoult's law can be applied to the water. Thus,

$$a_1 = x_{\text{H}_2\text{O},1} = 1 - x_{\text{CO}_2,1} \quad (22)$$

and this can be found directly from the solubility data at the pressure and temperature in question.

To estimate a_2 more accurately, define

a_2^* = the activity of water in NaCl aqueous solution without any dissolved carbon dioxide. These data are available.

a_2^{**} = the activity of water in solution of carbon dioxide without NaCl present.

Then, we assume that the activity of water in the NaCl- H_2O - CO_2 system can be expressed approximately by

$$a_2 = a_2^* a_2^{**} \quad (23)$$

Further, assume that Raoult's law can be applied to the solvent (water):

$$a_2^{**} = x_{\text{H}_2\text{O},2} = 1 - x_{\text{CO}_2,2} \quad (24)$$

With these assumptions, Equation (21) can be written as follows:

$$n = \frac{\ln f_2 / f_1}{\ln \left[(1 - x_{\text{CO}_2,1}) / a_2^* (1 - x_{\text{CO}_2,2}) \right]} \quad (25)$$

In practice, the terms $x_{\text{CO}_2,1}$ and $x_{\text{CO}_2,2}$ are found to be nearly equal, since the combination of the effects of higher pressure and higher salt concentration at state 2 tend to cancel each other and give nearly the same solubility at each state.

The detail of the calculation of a^* is presented in Appendix II. The P-V-T data for pure CO_2 and the calculation of the thermodynamic properties of CO_2 such as f and ΔH_{comp} , are also presented in Appendix III. With all the

terms known, n can be easily calculated from Equation (21).

This method requires sampling of the cell contents and determination of the salt concentration at each experimental point but one value of the composition of the hydrate is obtained for each point, thus giving some measurement of consistency. The results of this method are assumed to be more accurate than the method of de Forcrand. Also, they yield values of n at a range of temperatures and not just at the lower invariant point.

III. EXPERIMENTAL WORK

A. Experimental Apparatus

The apparatus used to determine the phase diagram of carbon dioxide hydrate consists of a reaction cell, a constant temperature bath, a refrigeration system, and measuring and controlling devices. A diagram of the entire system is shown in Figure 1.

The reaction cell is a Jerguson Large Chamber Gage No. 13-TL-10 and is a standard stock item used as a high pressure liquid level gauge. This cylindrical cell, having a volume of about 360 ml, is made of stainless steel. It is designed for a safe working pressure of 50 atm at 100°F; however, it has been tested at 100 atm and at room temperature by using a hand-operated hydraulic piston pump. The maximum pressure used in this work is approximately 45 atm (660 psia).

The cell has two windows, each 5-3/4 inch by 1/2 inch, through which one can observe the contents. Both ends of the cell are sealed and there are four outlets on one side of the cell. The first one is connected to the pressure gauge. The two in the middle are plugged and the last one is used for taking liquid samples. The reaction cell, weighing about twenty pounds, is supported by a trunnion designed to allow the cell to rotate through a 90° angle. A motor and cam connected to one end rocks the cell with an angle of 15° up and down for agitation.

The whole cell is immersed in the constant temperature bath which is provided with a heater and a cooling system. The temperature of the bath is controlled within $\pm 0.025^\circ\text{C}$ by a thermo cap control relay. The temperature is measured by a precision thermometer ranging from -20°C to $+20^\circ\text{C}$ with 0.1°C subdivision and calibrated against a calibrated thermometer (Brooklyn P-M Thermo Co. 13169) over the working range. A thermometer reader with 5X magnification is used.

The pressure measuring instrument is a Heise gauge having a range from 0 to 1000 psig with 1 psi subdivision. This gauge has been calibrated by the manufacturer. The average error is within ± 1 psi.

To minimize the volume of liquid remaining in the sampling line, a piece of 1/8 inch stainless steel tubing with the thickest wall available (0.035 inch) is used for taking samples. It is about 1 ml. All the valves, except a stainless steel sampling valve, are made of brass. Because of high pressure, the valves which are often used, e.g., valves A, C, D, E (see Figure 1), have to be changed every three or four months.

To avoid hydrate flushing out with solution while sampling, two pieces of 150 μ screen between which 0.5 cm thick of glass wool is tightly packed, are inserted in the connection between the sampling valve and the cell.

A light contained in a glass tube is set beneath the cell so that one can clearly observe the contents of the cell from the top of the bath without taking the cell out.

B. Experimental Procedures

The experimental work can be divided into three parts: (1) the equilibrium between carbon dioxide hydrate, liquid carbon dioxide and pure water; (2) the equilibrium between carbon dioxide hydrate, liquid carbon dioxide and gaseous carbon dioxide; and (3) the equilibrium between hydrate, gaseous carbon dioxide and NaCl aqueous solution. The first and second part of this experiment were performed to check Larson's data and our own techniques. The results came out very close to those of Larson.

1. The Equilibrium - $\text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s}) + \text{CO}_2(\text{l}) \rightleftharpoons \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$

From the phase rule in a two component-three phase equilibrium, the degree of freedom is only one. Once the temperature is fixed, the pressure of the system will be determined. These two variables can be measured directly from the pressure gauge and the thermometer.

The reactor was charged with approximately 90 ml of distilled water, and then the whole system evacuated for twenty minutes to get rid of air. To insure almost complete absence of air, carbon dioxide (99.95% bone dry grade) was introduced into the system which was then evacuated again.

The temperature was cooled down to -8°C to form ice. Carbon dioxide was then charged into the cell at pressures above its vapor pressure, until a desired amount of liquid carbon dioxide was obtained. Then the temperature was raised to melt the ice and the motor was turned on to mix the contents of the cell by rocking. Water combined with carbon dioxide to form white, transparent hydrate, as long as the temperature was below the critical decomposition temperature of 10.0°C . No liquid water phase was present and only three phases remained, i.e., liquid carbon dioxide, gaseous carbon dioxide and solid hydrate. Enough hydrate was formed so that the entire liquid phase would have hydrate crystals evenly distributed.

After the pressure reading was constant, the system was vented for one minute to reduce the pressure by about 50 psia. If the reading eventually returned to its initial value, the pressure and temperature were recorded. If not, this step was repeated to get rid of the impurity in the gaseous phase.

After the readings were recorded, the temperature was changed. It took about one to two hours to have a constant pressure reading, and the steps described above were repeated. A set of data was obtained as long as there were three phases inside the cell.

2. The Equilibrium - $\text{CO}_2(\text{g}) + n\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$

In this equilibrium, the degree of freedom is still one. The only difference is that the liquid phase is water instead of liquid carbon dioxide.

The cell was charged with approximately 180 ml of distilled water and the same procedures, as those described in the previous section, were used to get rid of air. Carbon dioxide was charged at 1°C and 440 psia. The contents were mixed vigorously by rocking the cell. Hydrate started to form about 10 minutes after charging and continued to form making the slurry difficult to mix. Finally, the contents could not be mixed and the water phase disappeared. This pressure of the system should be higher than the decomposition pressure.

The pressure was then released and every decrement was approximately 50 psia. After each reduction of pressure, the system was allowed to stand for a few minutes to see whether there was any increase in the pressure. An increase of pressure showed that the pressure of the system was below the decomposition pressure and the hydrate was decomposed.

When the decomposition pressure was reached, there were too many solids to have the contents well-mixed. The pressure was released again to decompose some of the hydrate crystals, until the desired amounts of solid and liquid were obtained. Too few solids in the liquid give a poor equilibrium because of lack of solid-liquid interfacial area. Too many solid particles give a mixture too stiff to be well agitated.

A sufficient amount of hydrate was initially formed in the cell to enable one to complete one run over the temperature range, -1.48°C to 10.0°C , without charging additional carbon dioxide.

3. The Equilibrium - $\text{CO}_2(\text{g}) + n\text{H}_2\text{O}(\text{l})$ in NaCl Solution $\rightleftharpoons \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$

In this equilibrium, there are three components and three phases. From the phase rule, the degrees of freedom are two. Once the temperature is fixed, the pressure of the system depends on the concentration of NaCl in the liquid phase. In this part of the experiment, the concentration of the liquid phase has to be measured by taking a sample of the aqueous liquid after equilibrium is established.

At the beginning of each run, the cell was charged with approximately 180 ml of NaCl aqueous solution. The same procedures were used to reach equilibrium. When the system is in equilibrium, the temperature and pressure readings were recorded. The sample was taken from valve G. The first 2 ml of solution were discarded and the sample was collected within ten seconds to prevent the decomposition of the hydrate.

The sample was divided into two or three parts, depending on the amount taken. Each part was weighed and the NaCl concentration was determined by the Mohr method, which uses silver chromate as an indicator in the titration of chlorides with silver nitrate solution. The average of the concentrations was taken as the concentration of the solution, if the deviation was within $\pm 1\%$.

After sampling, the temperature was raised and carbon dioxide was charged to the cell to maintain approximately constant concentration of the solution. It took about ten to twelve hours to reach equilibrium. In a report (R-5) by Bozzo, it is mentioned that if the temperature was lowered, it took a much longer time to reach equilibrium in the chlorine hydrate system.

When the volume of the liquid phase decreased to one half of the original volume, the run was terminated. A new solution was charged to the cell and a new run was started.

In this experiment the decomposition pressure of carbon dioxide hydrate in 5% and 10% NaCl solution, were measured. These results were used to calculate the hydrate composition.

IV. PRESENTATION AND ANALYSIS OF THE RESULTS

A. Experimental Data

All the experimental temperature-pressure-concentration data are listed in Tables 2, 3, 4 and 5.

B. Phase Diagram for CO₂-H₂O-Hydrate System

From the pressure-temperature data taken and the data of Larson (R-15) and Kennedy (R-31), a phase diagram for the CO₂-H₂O-hydrate system has been constructed in Figure 2.

In the phase diagram, there are five divariant areas and five univariant equilibrium curves. Each of the latter represents the equilibrium between three phases. There are two invariant points, A and B, each with four phases in equilibrium. Hydrate is stable in the areas to the left of the line segments EABC.

The lines AD, AB and BC have been measured by Larson. In this work, lines AD and AB are measured again. The data of Larson and this work are plotted on Figure 2. These data are then fitted to equations by the least squares method.

Line BC represents the equilibrium $\text{CO}_2(\text{g}) + n\text{H}_2\text{O}(\text{ice}) \rightleftharpoons \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$. Larson's data are fitted to the best two constant equation, i.e.,

$$\ln P(\text{atm}) = 13.50880616 - \frac{3036.897979}{T^\circ(\text{K})} \quad (26)$$

Line AD represents the equilibrium $\text{CO}_2(\text{g}) + \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CO}_2(\text{l}) + \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$. The equation based on the data taken in this work is:

$$\ln P(\text{atm}) = 10.75411787 - \frac{1971.035206}{T^\circ\text{K}} \quad (27)$$

The pressure of the system in this equilibrium should be the same as the vapor pressure of carbon dioxide, plus that of water which is negligible. The comparison of the values obtained from Equation (27), Larson's data and the vapor pressure of carbon dioxide (R-36) is shown in Table 6. The pressure deviations in this work are usually within ± 0.7 psi. It is believed that the pressure measurements in this work are more accurate than those in Larson's work.

Line AB (Fig. 2) represents the equilibrium $\text{CO}_2(\text{g}) + n\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$. The equation based on the data taken in this work from -1.5° to $+10^\circ\text{C}$, is:

$$\ln P(\text{atm}) = -58105.56177 + 8185.485312 \ln T + \frac{4,430,531.757}{T} - \frac{300,893.013}{T^2(^{\circ}\text{K})} \quad (28)$$

For the range from 9.015° to 10°C , this equilibrium is better expressed by:

$$\ln P(\text{atm}) = 50.11296571 - \frac{13114.74944}{T^\circ(\text{K})} \quad (29)$$

The experimental data curve a little sharply from 9° to 10°C and Equation (28) fits 7 points in this range with a deviation of ± 3 psi. It can be improved by adding more constants to Equation (28), but it is simpler to fit a separate equation, i.e. Equation (29). The following is the comparison of Equations (28) and (29), and the experimental data.

Temperature °C	Experimental Data (psi)	Values from Eq. (28) (psi)	Values from Eq. (29) (psi)
9.015	556.0	559.90	556.43
9.175	572.4	573.47	571.28
9.405	592.0	593.74	593.29
9.515	604.1	603.76	604.11
9.715	625.2	622.56	624.25
10.00	653.8	650.68	654.07
10.00	654.0	650.68	654.07
Avg. Dev. from Exptl. Pressures		2.3 psi	0.6 psi

These two equations intersect at 9.41°C. To calculate $Q = d\ln P/d(1/T)$, Equation (28) was used up to and including 9°C, and Equation (40) was used between 9° and 10°C. These four equations reproduced the experimental data with the following deviations in calculated pressure:

Equation No.	Average Deviation %	Maximum Deviation %
26	0.186	0.510
27	0.065	2.273
28	0.242	0.737
29	0.0995	0.218

Point A, the upper invariant point called the critical decomposition temperature, may be found from the intersection of Equation (27) with either Equation (28) or Equation (29). The former gives $t_c = 10.02^\circ\text{C}$ and the latter gives 9.99°C . We take t_c to be 10.00°C and the pressure at this point is the sum of the vapor pressures of CO_2 and H_2O , which from Equation (27) gives, $P_c = 44.40$ atm, or 652.5 psia. Point B, the invariant point with ice, is at -1.48°C and 10.28 atm (151.1 psia) and is found at the intersection of Equations (26) and (28). Larson reported these two points at 10.0°C , 653 psia and -1.5°C , 151 psia, respectively.

The following is a list of the reported values of the critical decomposition point:

Name of Worker	Temperature °C	Pressure (atm)
Villard (R-35)	10.0	44.3
Herreillers (R-13)	10.2	
Katz and Unruh (R-33)	9.89	44.42
Larson (R-15)	10.0	44.43
This work	10.00	44.40

The agreement among all these values is excellent.

Line BF (Fig. 2) represents the equilibrium between water, ice and gaseous carbon dioxide. On extension downward, it will reach 0°C when the pressure equals zero. It is below 0°C at 10 atm because of the depression of the freezing point of water by dissolved carbon dioxide.

Line AE in Figure 2 has been worked out by Takenouchi and Kennedy. It represents $\text{CO}_2(\text{l}) + n\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$ and may be considered as the effect of pressure on the melting point of CO hydrate. Their data are listed in Table 7. These data can be expressed by the following equation with an average deviation of 0.02% and at the worst 0.5%.

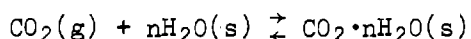
$$T(^{\circ}\text{K}) = 282.03 + 1.1392(\ln P) - 0.48547(\ln P)^2 + 0.069769(\ln P)^3 \quad (30)$$

where the unit of pressure is atm.

C. Composition of Carbon Dioxide Hydrate

1. de Forcrand's Method

By using Larson's data for the ice line equilibrium



and the data in Table 3, the carbon dioxide hydrate composition is determined by using de Forcrand's method, to be 5.93, which is only 2% less than Larson's value of 6.07. A detailed calculation of de Forcrand's method is presented in Appendix IV-A. Both the above values appear quite low compared to our work presented later.

2. Miller-Strong's Method

Six experimental runs have given a total of 57 data points of carbon dioxide hydrate in equilibrium with NaCl aqueous solution (see Table 4). Four of them are not suitable to use Miller-Strong's method, because the temperatures are lower than -1.48°C and the corresponding pressures on the CO_2 - H_2O -hydrate equilibrium line cannot be obtained. The other 53 points are used to calculate the hydrate composition by this method. A detailed sample calculation and the tabulated results are presented in Appendix IV-B and Table 13.

Runs IV, V and VI, considered to be more consistent and more reliable, give the hydrate composition of 7.25 ± 0.12 , 7.31 ± 0.11 and 7.33 ± 0.15 moles of water per mole of carbon dioxide, respectively. Taking the total average of these three runs gives the composition of carbon dioxide hydrate 7.30 ± 0.13 . This is taken to be the best value based on our data.

Runs I, II and III give a hydrate composition of 7.21 ± 0.18 , 7.06 ± 0.28 , and 7.54 ± 0.24 , respectively. These values are more scattered and are presumed unsuitable for averaging in with the reported value of the hydrate composition. Another reason for rejecting these is the improvement of the accuracy of titration for the later samples. In runs I, II and III, titration of two samples having the same concentration usually gave a deviation of 1 to 1.5%, but in runs IV, V and VI the deviation was generally less than 1%.

For chlorine hydrate, the composition is a function of temperature (R-37). In this work we attempted to note such a relationship for carbon dioxide hydrate, but no trend was observed over the range -1.5° to 10°C . It is probably because the composition is a weak function of temperature. Over the narrow range of 11° , the change is too small to be observed. In this work, one single value of the composition is reported for the working range.

There is a great difference between the values of the composition of CO_2 hydrate obtained by using the two methods described. Since there is no way to observe the consistency of the results when de Forcrand's method is used, the value 7.30, obtained from Miller-Strong's method, is recommended. Another reason is that we have to use the slope of the ice line in the de Forcrand method, but the equilibrium between ice hydrate and gaseous carbon dioxide is not easy to obtain. Larson probably didn't reach the true equilibrium.

D. Density of Carbon Dioxide Hydrate

The density of carbon dioxide hydrate can be calculated from the following equation (R-3):

$$\rho = 0.797 \left(1 + \frac{\text{M.W.}}{18n} \right) \left(\frac{12.00\text{\AA}}{\text{actual lattice constant}} \right)^3 \quad (31)$$

where M.W. is the molecular weight of carbon dioxide. The actual lattice constant is taken to be $12.04\text{\AA}$ (R-29). Based on $n = 7.3$, the density of the hydrate calculated from Equation (42) is 1.054 g/ml .

Takenouchi and Kennedy reported the density as 1.15 g/ml by using the Clausius-Clapeyron equation and Larson's ΔH° which is too high (see next section). If Larson's data with corrections are used, by the same method, the result comes out to be 1.112 g/ml . Takenouchi and Kennedy also mentioned that the density of carbon dioxide hydrate, as calculated from x-ray investigations, is 1.134 g/ml .

Here, the value 1.112 g/ml is recommended for the density of carbon dioxide hydrate. The value calculated from the thermodynamic relation is possibly more accurate than that from x-rays, but they differ by only 2%.

In our equilibrium cell with hydrate crystals distributed evenly throughout the liquid water phase, there were always gas bubbles mixed with the solids and it is difficult to note whether the hydrate sinks or floats, but when the liquid phase was carbon dioxide, the hydrate sank. The density of liquid carbon dioxide is 0.925 and 0.857 g/ml at temperatures 0°C and 10°C , respectively (R-16). Apparently, the density of the hydrate is greater than 0.925 g/ml .

E. Heats of Formation of Carbon Dioxide Hydrate

The method for calculating the heats of reaction from phase equilibrium

data has been given previously. By using the hydrate composition obtained from the Miller-Strong method, i.e $n = 7.30$, the heats of reaction of the four equilibria can be calculated.

For the equilibrium $\text{CO}_2(\text{g}) + n\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$, the heats of formation of the hydrate can be expressed as,

$$\Delta H^\circ = \Delta H_a + \Delta H_{\text{comp}} + s \Delta H_{\text{soln}} \quad (32)$$

where

$$\Delta H_a = - \left[V_s - V_g(1-s) - (n+s)V_L \right] \cdot \frac{P}{RT} Q \quad (33)$$

$$s = \frac{nx_{\text{CO}_2}}{1-x_{\text{CO}_2}} \quad (34)$$

V_s is the molar volume of the hydrate and can be calculated from its density. The density of the hydrate is taken to be 1.112 gm/ml. Thus,

$$V_s = 157.8 \text{ ml/gm-mole}$$

The detailed calculations are summarized in Table 8. It should be noted that ΔH° is not a constant. It decreases at first, then increases and finally decreases sharply. Larson has reported ΔH° by using van der Waal's equation to calculate the volume of gaseous carbon dioxide. van der Waal's equation is not very accurate at temperatures near the critical point, and at 8.5°C, gives a molar volume of carbon dioxide which is 10% higher than the experimental value. This is an unacceptable error for this type of calculation. The following is the comparison of our results, Larson's results and Larson's data with correction.

Temperature	Values of ΔH° (Kcal/g-mole)		Our Results
	Larson's Results	Larson's Data with Correction	
-1.5	14.4	14.03	14.25
3.9	15.8	14.83	14.43
8.5	16.3	14.79	14.40

The deviations are all less than 2.8% for the last two columns.

The calculated data on the variation of $-\Delta H^\circ$ with temperature show both a minimum at 0°C and a maximum at 7°C. It is unlikely that ΔC_p changes sign twice in the interval -1.5° to 10°C. In fact, we may make an educated guess as to the value of ΔC_p . The reaction involved is:



and

$$\Delta H^\circ = \Delta H_o + \int \Delta C_p dT$$

where

$$\Delta H_0 = \Delta H^\circ \text{ at the reference temperature}$$

$$\Delta C_p = C_p(\text{Hydrate}) - 7.3 C_p(\text{H}_2\text{O liquid}) - C_p(\text{CO}_2 \text{ gas}),$$

and the integration is taken over the interval from the reference temperature to the desired temperature.

The heat capacity of CO_2 gas increases only 0.09 cal/mole from 0 to 10°C and averages 8.66 cal/mole. Liquid water has a $C_p = 131.5$ cal for 7.3 moles. The only uncertainty is for the hydrate. Its heat capacity is certainly less than liquid water and probably much nearer that of ice. It may be a little greater than for ice (0.5 cal/gm) because the CO_2 molecules may be free to rotate in their cages. Guessing that C_p for the hydrate is then 0.6 cal/gm, one arrives at

$$\Delta C_p = -35 \text{ cal/gm-mole of hydrate}$$

In order for this ΔC_p to become positive, C_p for the hydrate would have to be greater than 0.8 cal/gm, which seems unlikely.

While the data do not agree with this, we have no way of improving our values of $-\Delta H^\circ$ at this time. We can say that the variation in ΔH° over the range -1.5° to $+10^\circ\text{C}$ is not likely to be greater than 400 cal/mole, that it probably is more negative at the higher temperature, and that the change is likely to be monotonic.

To be conservative it is recommended that the standard heat of formation of CO_2 hydrate from pure gaseous CO_2 at 1 atm and pure liquid water be taken as,

$$-\Delta H^\circ = 14.32 \text{ Kcal/gm-mole}$$

for the range -1.48 to 10°C .

For the equilibrium $\text{CO}_2(\text{g}) + n\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$, there are no solubility corrections necessary since the solubility of CO_2 in ice is negligible (R-26). The heat of reaction can be calculated from

$$\Delta H^\circ \approx ZR \frac{d \ln P}{d(1/T)} + \Delta H_{\text{comp}} \quad (35)$$

with the equation for this equilibrium, i.e. Equation (26). At the lower invariant point with ice

$$T = -1.48^\circ\text{C}$$

$$P = 10.28 \text{ atm}$$

$$V_G = 2.0051 \text{ l/g-mole}$$

$$Z = 0.9246$$

$$\Delta H_a = -5.58 \text{ Kcal/g-mole}$$

$$\Delta H_{\text{comp}} = -0.144 \text{ Kcal/g-mole}$$

and

$$\Delta H^\circ = -5.72 \text{ Kcal/g-mole} \quad (36)$$

For the equilibrium $\text{CO}_2(\text{g}) + \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CO}_2(\text{l}) + \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$, the heat of reaction is equal to the heat of condensation of carbon dioxide. The same method can be used to calculate the heat of reaction at critical decomposition point.

$$T = 10.00^\circ\text{C}$$

$$P = 44.40 \text{ atm}$$

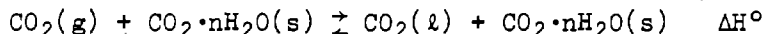
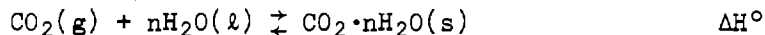
$$V_G = 0.3271 \text{ l/g-mole} \quad V_L = 0.0513 \text{ l/g-mole} \quad (\text{R-16})$$

$$\begin{aligned} \Delta H_a &= - \left[V_L - V_G \right] \frac{P}{RT} \cdot \left(R \cdot \frac{d \ln P}{d(1/T)} \right) \\ &= -2.07 \text{ Kcal/g-mole} \end{aligned}$$

This may be compared with the value -2.12 in the literature (R-16). Then:

$$\Delta H^\circ = \Delta H_a + \Delta H_{\text{comp}} = -2.80 \text{ Kcal/g-mole} \quad (37)$$

For the equilibrium $\text{CO}_2(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$, the heat of reaction can be calculated from ΔH_1° and ΔH_2° , the heats of reaction of the following two reactions, respectively:



At $T = 10.00^\circ\text{C}$,

$$\Delta H^\circ = \Delta H_1^\circ - \Delta H_2^\circ = (-13.89) - (-2.80) = -11.09 \text{ Kcal/g-mole hydrate} \quad (38)$$

On the basis of one pound of water,

$$\Delta H = \frac{11.09 \times 10^3 \times 1.8}{n \cdot (\text{M.W.}_{\text{H}_2\text{O}})} = 152 \text{ Btu/lb. H}_2\text{O solidified} \quad (39)$$

The value of n used here is 7.30. ΔH has a value of 152 Btu/lb. H_2O , which may be compared with the heat of fusion of ice, 144 Btu/lb.

F. Phase Diagram for CO_2 -NaCl Solution-Hydrate System

From the pressure-temperature data taken, a phase diagram for the CO_2 -NaCl solution-hydrate system is given in Figure 3. Also, from the critical points measured for NaCl solution of various concentrations (see Table 5), a figure showing the effect of concentration on critical temperature has been constructed (see Figure 4).

The effect of the NaCl concentration on critical decomposition temperature of CO₂ hydrate can be expressed by the following equation:

$$C = 0.05286 (10.0 - t)(t + 29.361) \quad (40)$$

Equation (40) reproduces the experimental data with an average deviation of 2.11% and a maximum of 5.69%. It should not be used for extrapolation beyond 16% NaCl.

A line predicted for the critical decomposition temperature vs concentration of sea salts is also shown in Figure 4 by using the following relations (R-3):

$$a_{H_2O}(\text{in NaCl solution}) = a_{H_2O}(\text{in sea salt solution}) \quad (41)$$

when

$$0.927 \cdot (\text{wt.}\% \text{ sea salt}) = \text{wt.}\% \text{ NaCl} \quad (42)$$

This line is useful in a practical application of desalting sea water.

Figures 2, 3 and 4 do not give sufficient information for engineering use, if CO₂ is to be used as the hydrating agent in the hydrate process to separate fresh water from sea water. By assuming the hydrating number $n = 7.30$ and using Miller-Strong's method in reverse, a set of pressure-temperature-concentration data is obtained and tabulated in Table 9. From these data, one can easily construct the phase diagram for the CO₂-NaCl solution-hydrate system. The data can be converted for use with sea water by dividing the % NaCl by 0.927 to give wt.% sea salts.

G. Complete Known Phase Diagram for Carbon Dioxide Hydrate

A complete known phase diagram has been plotted in Figure 5. The following is a list of the data sources:

<u>Line</u>	<u>Data taken from</u>
AB, A'B', A''B'', AD	This work
BC	Larson (R-15)
AE	Takenouchi and Kennedy (R-31)
KD, DJ	Vukalovich and Altumn (R-36)
GH	Miller and Smythe (R-19)

In the diagram point D, 216.55°K and 5.112 atm, is the triple point of pure carbon dioxide. Line KD is the equilibrium line of solid CO₂ and liquid CO₂. Line AE, the equilibrium CO₂(l) + nH₂O(l) ⇌ CO₂·nH₂O(s), has about the same shape as line KD; that is, the effect of pressure on the melting point of solid CO₂ is very similar to its effect on the melting point of the hydrate. Line BF will reach 0°C as the pressure goes to zero. This line represents the depression of the freezing point of water due to dissolved CO₂. Miller and Smythe predict that lines GH and DJ will intersect at 121.22°K and 2.481x10⁻⁴ atm (0.2 mm Hg).

Lines A'B' and A"B" are drawn for NaCl solutions of approximately 5 and 10 wt. %.

No data are available for the lines shown dotted.

H. The Eutectic Point of CO₂-H₂O-NaCl System

The determination of the eutectic point of hydrate system with salts present is important for a eutectic hydrate process for separating saline solutions into water and solid salt with no brine product. The eutectic point determines the conditions at which the process must operate. From the experimental results, the eutectic point at which five phases, i.e., CO₂(g), CO₂(l), hydrate, NaCl·2H₂O and saturated aqueous solution would exist is determined to be at -9.6°C and a pressure of 389 psia with the aqueous solution containing 24.2 per cent NaCl.

The apparatus used in this experiment is the same as that used for determination of the CO₂ hydrate phase diagram. Additional data on the depression of the critical decomposition temperature of CO₂ hydrate by NaCl were taken and are plotted on Figures 6 and 7 and listed in Table 5. Each of the data points represents an equilibrium in which four phases, i.e., CO₂(g), CO₂(l), hydrate and NaCl solution are present. The effect of the NaCl concentration on the critical temperature can be expressed by the following equation:

$$C = + 0.00098241 (10-t) (t^2 + 45.385t + 1588.75)$$

The above equation reproduces the experimental concentrations with an average deviation of 1.33% and a maximum of 5.61%. For example, using the average deviation, the calculated value of C at $t = 0^\circ\text{C}$ would be $15.61 \pm 0.21\%$ NaCl.

To determine the decomposition pressure of CO₂ hydrate in the saturated NaCl solution, four phases, CO₂(g), hydrate, NaCl·2H₂O and NaCl saturated solution must co-exist. At first, about 30 gm of NaCl was put into the reaction cell. Then saturated NaCl solution was charged until three quarters of the cell volume was filled. The cell was put into the constant temperature bath and rocked at -14°C for at least 36 hours to mix the contents so that the NaCl crystals will not cake. It is presumed that all the NaCl crystals transformed to NaCl·2H₂O, the hexagonal dihydrate crystal, but, unfortunately, it is impossible to tell by looking at them whether the crystals that are present are NaCl or NaCl·2H₂O.

The same procedures that were used to obtain the equilibrium between CO₂(g), hydrate and NaCl solution were used here to reach the equilibrium. The only difference is that instead of three phases, four phases, i.e., CO₂(g), hydrate, NaCl·2H₂O and NaCl solution were present at equilibrium. It is easy to distinguish between CO₂ hydrate and NaCl dihydrate, since the CO₂ hydrate floats and the dihydrate sinks. The data are plotted on Figure 7 and listed in Table 11.

In Figure 7, the intersection between the two equilibrium lines AD on which CO₂(l), CO₂(g), hydrate and NaCl solution are in equilibrium and DG on which CO₂(g), hydrate, NaCl·2H₂O and NaCl saturated solution are in equilibrium is at -9.6°C and 389 psia with NaCl concentration 24.2 per cent. Since this value is determined solely by pressure and temperature measurements and do not depend on the determination of NaCl concentration that is less accurate, this value is considered to be more accurate than the one determined in Figure 6. These two methods of determination of the eutectic temperature should, of

course, give the same value. The intersection on Figure 6 is at -10.0°C but this depends critically on the NaCl analysis and is presumed less accurate than that determined on Figure 7. We thus take the hydrate eutectic conditions for the system CO_2 hydrate in aqueous NaCl solutions to be -9.6°C , 389 psia and 24.2% NaCl in the aqueous phase.

V. SUMMARY

An apparatus in which temperature can be controlled within $\pm 0.025^{\circ}\text{C}$ and pressure can be measured to ± 1 psia was used to measure the various equilibria involving CO_2 hydrate. The pressure-temperature-concentration data for CO_2 hydrate-NaCl solution system with temperatures ranging from -10°C to 10°C , pressures from 10 to 50 atm and concentrations from 0 to 10% NaCl, were accurately measured. Also, the eutectic present with NaCl was found.

The composition of the hydrate was then determined from 31 experimental points, by the Miller-Strong method, to be 7.30 ± 0.13 moles of water per mole of hydrate. Based on $n = 7.30$, the heats of formation of carbon dioxide hydrate were calculated. Also, by using the Miller-Strong method in reverse, a set of tabulated P-T-C data has been presented to enable one to construct a phase diagram for CO_2 -hydrate-NaCl solution system. The eutectic point at which CO_2 gas and liquid, CO_2 hydrate, NaCl $2\text{H}_2\text{O}$ and saturated aqueous solution are present was found to occur at $t = -9.6^{\circ}\text{C}$, $P = 389$ psia and $C = 24.2$ wt.% NaCl.

A complete summary of the critical decomposition constants, heats of reaction, composition and temperature depression due to NaCl for carbon dioxide hydrate, is given in Table 10.

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VII. NOMENCLATURE

a	= activity
A	= hydrating agent, CO_2
AB_n	= hydrate, $\text{CO}_2 \cdot n\text{H}_2\text{O}$
B_i, C_i	= constants
C	= concentration
f	= fugacity
G	= gas phase
h	= molar enthalpy for pure substance
$\bar{h}$	= partial molar enthalpy
h°	= molar enthalpy in the standard state
ΔH_a	= actual enthalpy change of reaction between phases
ΔH_{comp}	= heat of compression = $\bar{h}_{A,G} - h^\circ_{A,G}$
ΔH_{fusion}	= heat of fusion of ice
ΔH_{soln}	= heat of solution
ΔH°	= enthalpy in the standard state
K	= equilibrium constant
L	= liquid
n	= hydrating number (moles of water per mole of hydrate)
P	= pressure
Q	= $R \frac{d(\ln P)}{d(1/T)}$
r	= number of moles of water which vaporize when one mole of hydrate decomposes
R	= gas constant
s	= number of moles of hydrating agent which dissolve in the liquid phases when one mole of hydrate decomposes, solid phase
t	= temperature in $^\circ\text{C}$
T	= absolute temperature

NOMENCLATURE (Cont'd.)

V	= molar volume of a pure substance
$\bar{V}$	= partial molar volume
V_G, V_L, V_{AB_n}	= molar volume of gas phase, liquid phase and hydrate, respectively
ΔV_a	= actual volume change of reaction between phases
x	= mole fraction in the liquid phase
y	= mole fraction in the gaseous phase
Z	= compressibility factor
μ	= chemical potential of a component in a mixture
μ°	= chemical potential for pure substance
Subscript 1	= in the pure water system
Subscript 2	= in the NaCl solution system

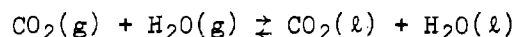
TABLE 1 - The Reported Compositions of CO₂ Hydrate

Names of the Workers	Method Used	Hydrate Composition mole H ₂ O/mole CO ₂	Year
Wroblewski	Direct analysis	8	1882
Villard	Direct analysis	6	1897
Hempel and Seidel	Direct analysis	8 or 9	1898
de Forcrand	Thermodynamic method	6	1902
Bouzat and Azinieres	Assume CO ₂ hydrate to be similar to Cl ₂ hydrate	6	1924
Frost and Daton	Direct analysis	7	1946
Claussen	X-ray analysis	$5\frac{3}{4}$	1951
Larson	Thermodynamic method	6.07	1955

TABLE 2 - Equilibrium Pressures for
 $\text{CO}_2(\text{g}) + \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CO}_2(\text{l}) + \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$

Temperature(°C)	Pressure(psia)	Temperature(°C)	Pressure(psia)
-10.1	383.6	1.905	531.4
- 9.11	394.1	1.945	532.1
- 9.045	395.1	2.03	532.9
- 9.035	395.5	2.08	533.9
- 8.55	400.6	3.90	559.6
- 8.0	406.6	4.11	563.5
- 7.5	412.6	4.80	573.6
- 7.0	418.3	4.95	574.4
- 6.884	419.5	4.98	575.2
- 6.03	429.6	5.0	575.1
- 6.0	430.1	5.98	590.5
- 5.32	438.1	7.885	619.1
- 5.0	441.7	7.915	619.8
- 4.875	443.5	8.07	622.9
- 4.02	454.1	8.485	628.2
- 3.997	454.5	8.88	635.1
- 3.045	466.0	8.985	635.7
- 2.935	467.2	9.87	650.1
- 2.145	477.4	10.035	651.5
- 2.01	479.2	10.085	652.2
- 1.971	479.4	10.475	660.1
- 0.87	493.8	11.46	676.1
- 0.03	504.9	11.98	683.6
- 0.016	505.3	13.88	718.1
0.0	505.0	14.864	733.6
0.965	518.7	14.874	734.6
1.08	519.5	14.89	736.2

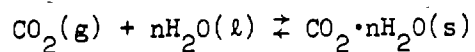
Above 10°C, the three phases were $\text{CO}_2(\text{l})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$. The equilibrium became



The density of liquid carbon dioxide is less than the density of liquid water at these temperatures. The top layer of the two liquid phases is liquid carbon dioxide.

In the range 0 to 15°C the vapor pressure of water is only 0.02 to 0.03% of that of CO_2 , and the equilibrium done is entirely controlled by the vapor pressure of CO_2 .

TABLE 3 - Hydrate Decomposition Pressures for



Temperature(°C)	Pressure(psia)	Temperature(°C)	Pressure(psia)
- 1.549	150.8	4.506	303.5
- 1.449	151.6	4.64	308.5
- 1.445	151.3	4.97	323.5
- 1.13	157.8	5.50	344.0
- 1.02	159.0	5.58	348.0
- 0.845	162.0	5.62	349.7
- 0.46	168.7	6.00	368.5
- 0.07	176.7	6.584	397.0
- 0.054	177.3	6.954	417.5
0.50	188.5	7.254	433.5
0.763	194.7	7.585	454.5
1.045	201.1	8.006	482.5
1.51	212.0	8.286	503.4
1.56	213.5	8.626	525.9
2.12	227.6	8.695	533.7
2.554	239.5	9.015	556.0
2.965	252.6	9.175	572.4
3.412	267.5	9.405	592.0
3.525	268.2	9.515	604.1
3.847	279.5	9.715	625.2
4.008	287.6	10.00	653.8
4.087	287.7	10.00	654.0

At 10°C there were four phases, i.e. $\text{CO}_2(\text{g})$, $\text{CO}_2(\text{l})$, $\text{H}_2\text{O}(\text{l})$ and $\text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$.

TABLE 4 - Hydrate Decomposition Pressures for
 $\text{CO}_2\text{-NaCl-H}_2\text{O-Hydrate System}$
 $\text{CO}_2(\text{g}) + n\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$

Point No.	Temperature(°C)	Pressure(psia)	Wt.% NaCl
Run I	1 2.974	333.2	5.42
	2 4.017	376.5	5.28
	3 6.00	488.9	5.30
	4 6.42	503.0	4.865
	5 6.843	562.3	5.37
Run II	6 2.723	313.0	5.27
	7 3.235	338.3	5.72
	8 3.847	367.5	5.76
	9 4.348	405.4	5.80
	10 4.779	418.5	5.545
	11 5.48	468.6	5.445
	12 6.18	511.9	5.45
	13 6.552	540.6	5.53
Run III	14 -1.545	191.3	4.79
	15 -1.06	202.8	5.215
	16 -0.56	217.8	5.375
	17 -0.02	230.5	5.26
	18 0.50	247.9	5.385
	19 0.915	251.9	4.665
	20 1.50	279.5	5.715
	21 2.13	292.7	4.81
	22 7.214	613.0	5.875
Run IV	23 -1.535	251.6	10.17
	24 -0.53	293.6	10.33
	25 0.01	303.8	10.30
	26 1.015	345.7	10.31
	27 1.54	384.5	10.50
	28 2.02	404.1	10.30
	29 2.533	440.9	10.46
	30 3.004	462.0	10.26
	31 3.565	498.0	10.37
	32 4.027	524.9	10.27
	33 4.227	546.3	10.21
Run V	34 -5.00	172.5	10.59
	35 -4.018	194.2	10.55
	36 -3.03	215.8	10.38
	37 -2.09	239.1	10.22
	38 -0.967	278.4	10.25
	39 0.52	327.9	10.22
	40 1.37	360.8	10.20
	41 2.152	419.5	10.32
	42 2.222	417.4	10.30
	43 3.164	468.9	10.19
	44 3.345	483.4	10.29
	45 3.776	501.0	10.16
	46 3.796	517.4	10.41
	47 4.047	533.9	10.20

(Cont'd.)

TABLE 4 (Cont'd.)

Point No.	Temperature(°C)	Pressure(psia)	Wt.%Nacl
Run VI 48	0.03	239.8	5.871
49	1.035	270.5	5.917
50	1.921	298.2	5.834
51	3.025	341.5	5.764
52	3.455	370.5	6.132
53	3.998	388.0	5.733
54	4.578	420.5	5.860
55	5.06	445.5	5.949
56	5.53	467.3	5.632
57	6.01	498.7	5.568

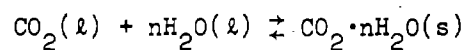
TABLE 5 - NaCl EFFECT ON THE CRITICAL DECOMPOSITION TEMPERATURE
OF CARBON DIOXIDE HYDRATE

Temperature t°C	Pressure psia	Concentration wt.% NaCl	Temperature t°C	Pressure psia	Concentration wt.% NaCl
8.94	635.8	2.28	1.34	486.9	16.94
8.79	633.5	2.35	- 1.44	486.7	17.19
7.52	613.5	5.05	- 1.49	485.7	17.21
7.31	610.2	5.23	- 3.68	457.7	19.47
7.08	606.8	5.38	- 3.75	456.9	19.48
5.78	587.9	8.00	- 4.05	452.8	19.73
5.53	583.4	8.20	- 4.44	448.2	20.07
5.36	580.3	8.14	- 4.62	446.6	20.33
5.00	576.4	8.90	- 4.87	443.9	20.42
4.75	571.8	9.98	- 5.10	440.5	20.69
4.13	563.4	10.25	- 5.32	437.6	21.02
4.00	561.9	10.37	- 5.63	434.5	21.18
3.84	559.0	10.53	- 5.80	432.6	21.28
3.44	553.6	11.09	- 6.00	429.9	21.42
0.66	514.1	14.94	- 6.27	426.4	21.64
0.64	514.3	14.94	- 6.55	423.5	21.92
0.52	512.3	15.20	- 6.60	423.1	21.47
0.48	512.7	15.16	- 6.80	420.7	21.72
0.20	508.4	15.34	- 8.60	399.2	23.45
0.20	508.6	15.28	- 8.80	397.6	23.50
0.03	506.0	15.56	- 8.90	396.6	23.58
- 0.07	504.8	15.57	- 9.00	395.2	23.63
- 0.23	501.7	15.94	- 9.28	391.9	23.83
- 0.56	498.6	16.39	- 9.50	388.7	23.99
- 0.56	498.1	16.38	- 9.73	387.1	23.74
- 0.82	494.6	16.02	- 9.92	385.1	24.08
- 0.92	493.7	16.20	- 9.97	384.6	23.89
- 1.16	490.2	16.75	- 10.08	383.0	24.21
			- 10.40	381.1	24.11

TABLE 6 - Comparison of the Equilibrium Pressures for
 $\text{CO}_2(\text{g}) + \text{CO}_2 \cdot \text{nH}_2\text{O}(\text{s}) \rightleftharpoons \text{CO}_2(\text{l}) + \text{CO}_2 \cdot \text{nH}_2\text{O}(\text{s})$

Temperature °C	P1 Vapor Pressure of Pure CO_2 (psi)(R-36)	P2 Equilibrium Pressure from Equation (38)(psi)	P3 Equilibrium Pressure from Larson's data (psi)	P1-P2 psi	P1-P3 psi
-10.7	376.3	376.7	377	-0.4	-0.7
- 9.4	390.5	390.9	391	-0.4	-0.5
- 8.3	402.8	403.3	403	-0.5	-0.2
- 5.9	430.6	431.1	431	-0.5	-0.4
- 3.0	466.0	466.7	467	-0.7	-1.0
- 1.1	490.4	491.1	491	-0.7	-0.6
1.2	521.2	521.8	521	-0.6	0.2
3.1	547.7	548.2	548	-0.5	-0.3
5.7	585.6	586.0	586	-0.4	-0.4
8.3	625.4	625.5	626	-0.1	-0.6
9.9	650.9	650.8	651	0.1	-0.1
10.3	657.4	657.2	656	0.2	1.4
11.3	673.8	673.4	673	0.4	0.8
11.8	682.2	681.7	681	0.5	1.2
Avg. Deviation in psi				0.43	0.6

TABLE 7 - Hydrate Decomposition Pressures from Takenouchi and Kennedy



Temperature(°C)	Pressure(psia)	Temperature(°C)	Pressure(psia)
10.0	652.7	16.0	12,778.0
10.5	1,232.8	17.0	15,881.9
11.0	1,885.5	17.5	17,694.9
11.5	2,639.7	18.0	19,623.9
12.0	3,524.5	18.5	21,654.5
13.0	5,395.5	19.0	23,946.1
14.0	7,571.1	19.5	27,006.4
15.0	10,094.8		

TABLE 8 - Heat of Formation Calculations for Carbon Dioxide Hydrate in
 $\text{CO}_2(\text{g}) + n\text{H}_2\text{O}(\ell) \rightleftharpoons \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$

Temp. °C	P (atm)	Q (Kcal/g-mole)	V _G (ℓ/g-mole)	x _{CO₂}	s = $\frac{nx}{1-x}$	ΔH _a (Kcal/g-mole)	ΔH _{comp} ($\frac{\text{Kcal}}{\text{g-mole}}$)	sΔH _{soln} ($\frac{\text{Kcal}}{\text{g-mole}}$)	ΔH° ($\frac{\text{Kcal}}{\text{g-mole}}$)
-1.48	10.277	-16.603	2.0052	0.01347	0.099474	-13.63	-0.14378	-0.473	-14.247
-1	10.851	-16.647	1.8944	0.01399	0.10358	-13.538	-0.15128	-0.49252	-14.182
0	12.151	-16.827	1.6815	0.01492	0.11057	-13.42	-0.16829	-0.52576	-14.114
1	13.619	-17.123	1.4891	0.01578	0.11704	-13.378	-0.18759	-0.55653	-14.122
2	15.278	-17.536	1.3152	0.01659	0.12315	-13.398	-0.20959	-0.58558	-14.193
3	17.198	-18.063	1.1548	0.01745	0.12965	-13.449	-0.23546	-0.61649	-14.301
4	19.407	-18.704	1.0084	0.01843	0.13707	-13.507	-0.26586	-0.65177	-14.425
5	21.98	-19.458	0.8737	0.01923	0.14313	-13.582	-0.30249	-0.68058	-14.565
6	25.002	-20.322	0.7493	0.02025	0.15088	-13.588	-0.3475	-0.71743	-14.653
7	28.583	-21.297	0.634	0.0209	0.15583	-13.548	-0.40434	-0.74097	-14.693
8	32.86	-22.38	0.5266	0.0219	0.16345	-13.296	-0.47849	-0.77720	-14.552
9	37.769	-23.571	0.4301	0.02234	0.16681	-12.88	-0.57391	-0.79318	-14.248
10	44.40	-26.062	0.3271	0.02255	0.16841	-12.356	-0.72957	-0.80079	-13.886

TABLE 9 - Calculated Pressure-Temperature-Concentration
Data for CO₂-NaCl Solution-Hydrate System with n = 7.3

Temperature °C	Pressure in atm. for NaCl Solutions						
	0%	2.5%	5%	7.5%	10%	12.5%	15%
-1.48	10.277	11.49	12.959	14.808	17.227	20.527	25.262
0	12.151	13.613	15.397	17.663	20.672	24.866	31.125
1	13.619	15.282	17.322	19.935	23.448	28.444	
2	15.287	17.187	19.531	22.563	26.701	32.749	
3	17.198	19.379	22.090	25.641	30.583		
4	19.407	21.928	25.091	29.301	35.335		
5	21.98	24.919	28.657	33.745			
6	25.002	28.475	32.967	39.305			
7	28.583	32.746	38.30				
8	32.86	37.98					
9	37.769						
10	44.40						
Critical Temp. °C	10.00	8.80	7.54	6.16	4.60	2.82	0.81

TABLE 10 - Critical Decomposition Constants, Heats of Reaction, Composition, and Temperature Depression Due to NaCl for Carbon Dioxide Hydrate

1.	Hydrate Composition (n) moles H ₂ O/mole CO ₂		7.30 ± 0.13
2.	Critical Decomposition Temperature, °C °F		10.00 50.0
3.	Critical Decomposition Pressure, atm psia		44.40 652.5
4.	Invariant Point with Ice, Temperature °C atm		-1.48 10.28
5.	Constants in Empirical Equations		
	a) CO ₂ (g) + nH ₂ O(l) ⇌ CO ₂ ·nH ₂ O(s)		
	Line AB - Figure 2	A	-58,105.56177
	lnP(atm) = A+B lnT + $\frac{C}{T}$ + $\frac{D}{T^2}$	B	8,185.485312
		C	4,430,531.757
		D	-300,893,013
	b) CO ₂ (g) + CO ₂ ·nH ₂ O(s) ⇌ CO ₂ (l) + CO ₂ ·nH ₂ O(s)		
	Line AD - Figure 2	A	10.75411787
	lnP(atm) = A-B/T(°K)	B	1971.035206
	c) CO ₂ (g) + nH ₂ O(s) ⇌ CO ₂ ·nH ₂ O(s)		
	Line BC - Figure 2	A	13.50880616
	lnP(atm) = A-B/T(°K)	B	3036.897979
6.	Compressibility Factor of CO ₂ at upper Critical Decomposition Temperature and Pressure (Z)		0.625
7.	Heats of Reaction (uncorrected)		
	a) CO ₂ (g) + nH ₂ O(l) = CO ₂ ·nH ₂ O(s) (Kcal/mole at 10.00°C)		13.16
	b) CO ₂ (g) + CO ₂ ·nH ₂ O(s) = CO ₂ (l) + CO ₂ ·nH ₂ O(s) (Kcal/mole at 10.00°C)		2.07
	c) CO ₂ (g) + nH ₂ O(s) = CO ₂ ·nH ₂ O(s) (Kcal/mole at -1.48°C)		5.72

TABLE 10 (Cont'd.)

d)	$\text{CO}_2(\text{l}) + \text{nH}_2\text{O}(\text{l}) = \text{CO}_2 \cdot \text{nH}_2\text{O}(\text{s})$ (Btu/lb. H_2O at 10.00°C)	152
8.	Depression of Critical Decomposition Temperature by NaCl , $^\circ\text{C}$	
	2%	0.99
	4%	2.03
	6%	3.13
	8%	4.32
	10%	5.60
	12.5%	7.40
	15%	9.50
9.	Depression of Critical Decomposition Temperature $^\circ\text{F}$ by a 6% sea salt solution $^\circ\text{C}$	5.18 2.88
10.	Hydrate Reactor Operating Conditions Allowing 3°F for Driving Force in 6% sea salt solutions	
	temperature, $^\circ\text{F}$	41.9
	pressure, psig	595

TABLE 11 - DECOMPOSITION PRESSURES OF CO₂ HYDRATE IN SATURATED NaCl SOLUTION
(PHASES PRESENTS ARE CO₂(g), HYDRATE, NaCl·2H₂O(s), NaCl SOLUTION)

<u>Temperature</u> (°C)	<u>Pressure</u> (psia)	<u>NaCl Concentration</u> (wt.%) in solution
- 14.32	190.6	
- 13.70	208.1	
- 13.60	210.8	
- 13.22	222.5	
- 13.10	226.1	
- 12.96	229.3	23.6
- 12.80	236.5	23.8
- 12.63	241.1	
- 12.50	247.4	
- 12.15	264.9	
- 12.13	263.4	24.1
- 11.82	272.0	
- 11.57	282.3	24.3
- 11.12	297.8	
- 11.12	298.5	
- 10.77	320.4	24.3
- 10.54	333.4	24.2
- 10.35	341.3	
- 10.25	347.7	
- 10.16	351.3	24.3
- 10.02	361.6	24.3
- 9.80	371.6	24.3
- 9.68	380.4	24.2

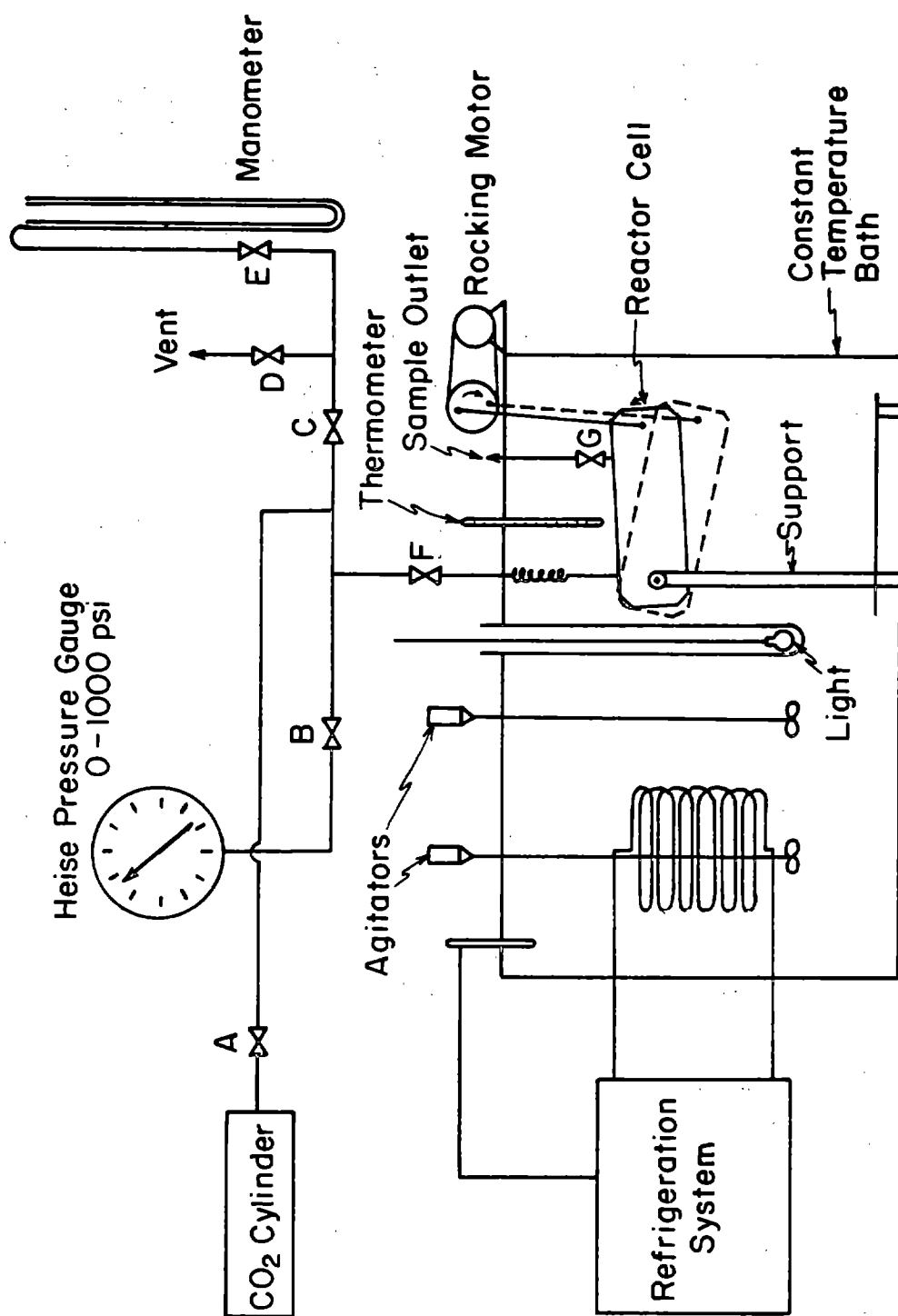


FIG. 1 EXPERIMENTAL APPARATUS

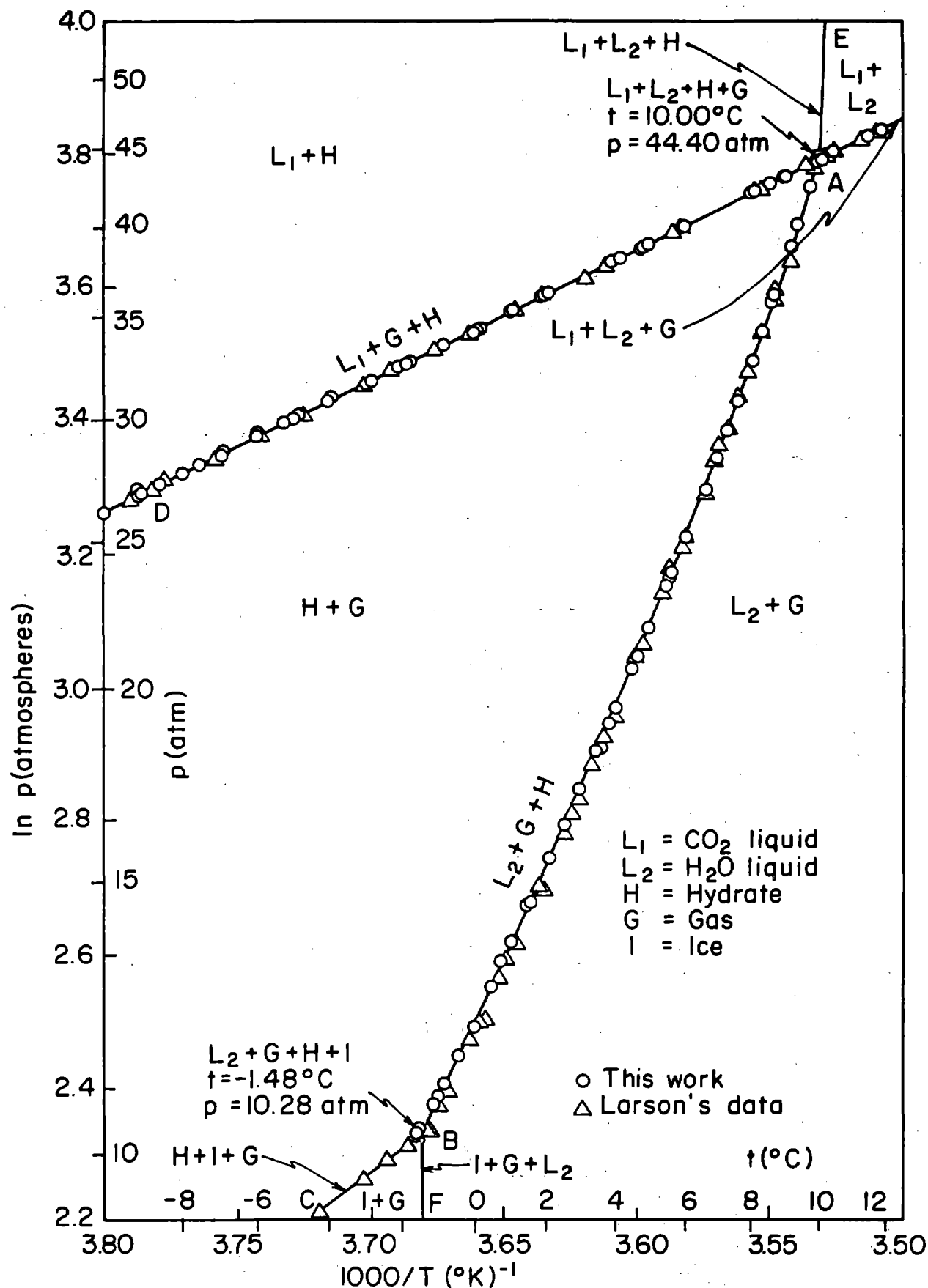


FIG. 2 EXPERIMENTAL PHASE DIAGRAM FOR CO₂-H₂O-HYDRATE SYSTEM

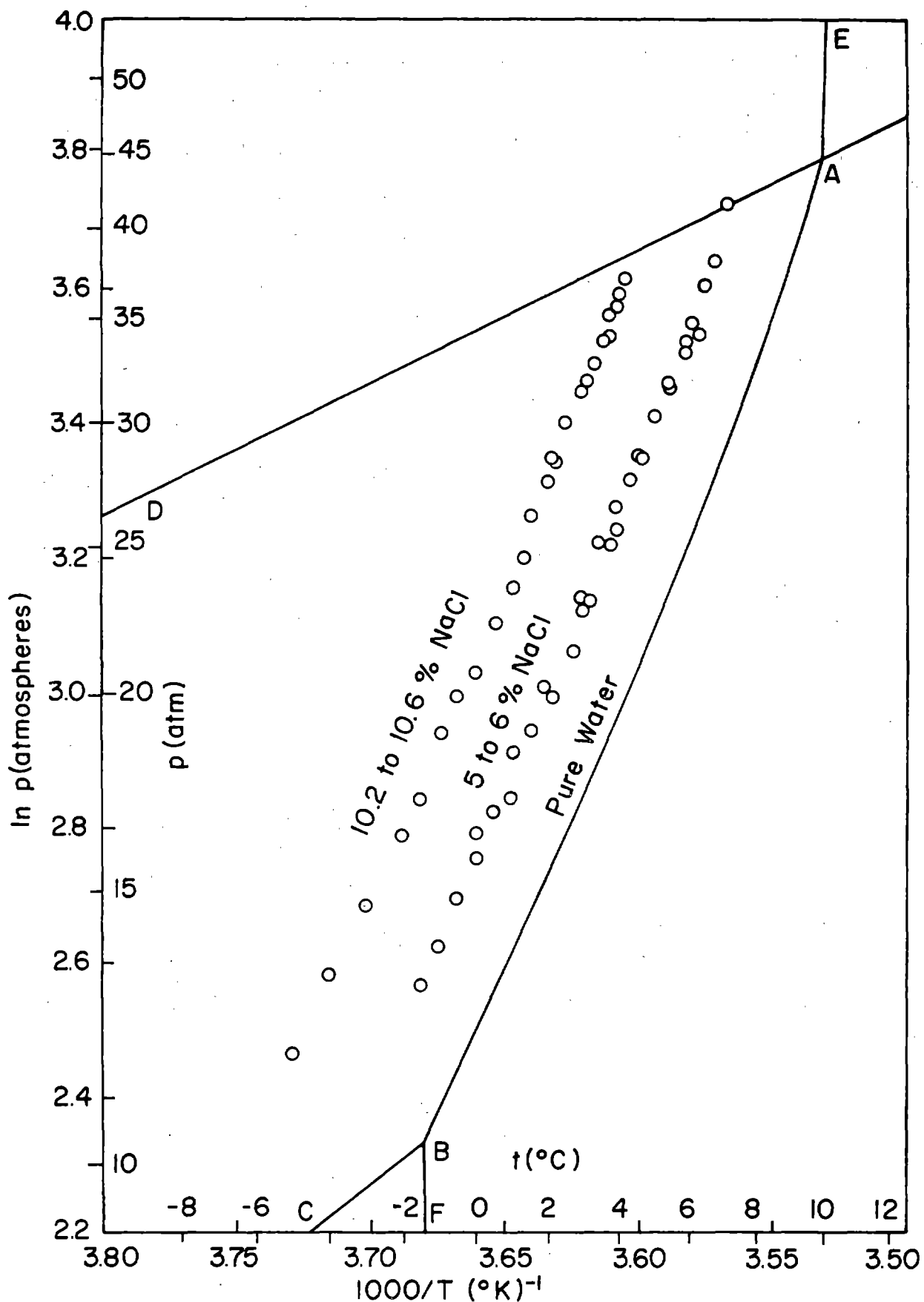


FIG. 3 EXPERIMENTAL PHASE DIAGRAM FOR $\text{CO}_2\text{-NaCl-H}_2\text{O}$ -HYDRATE SYSTEM

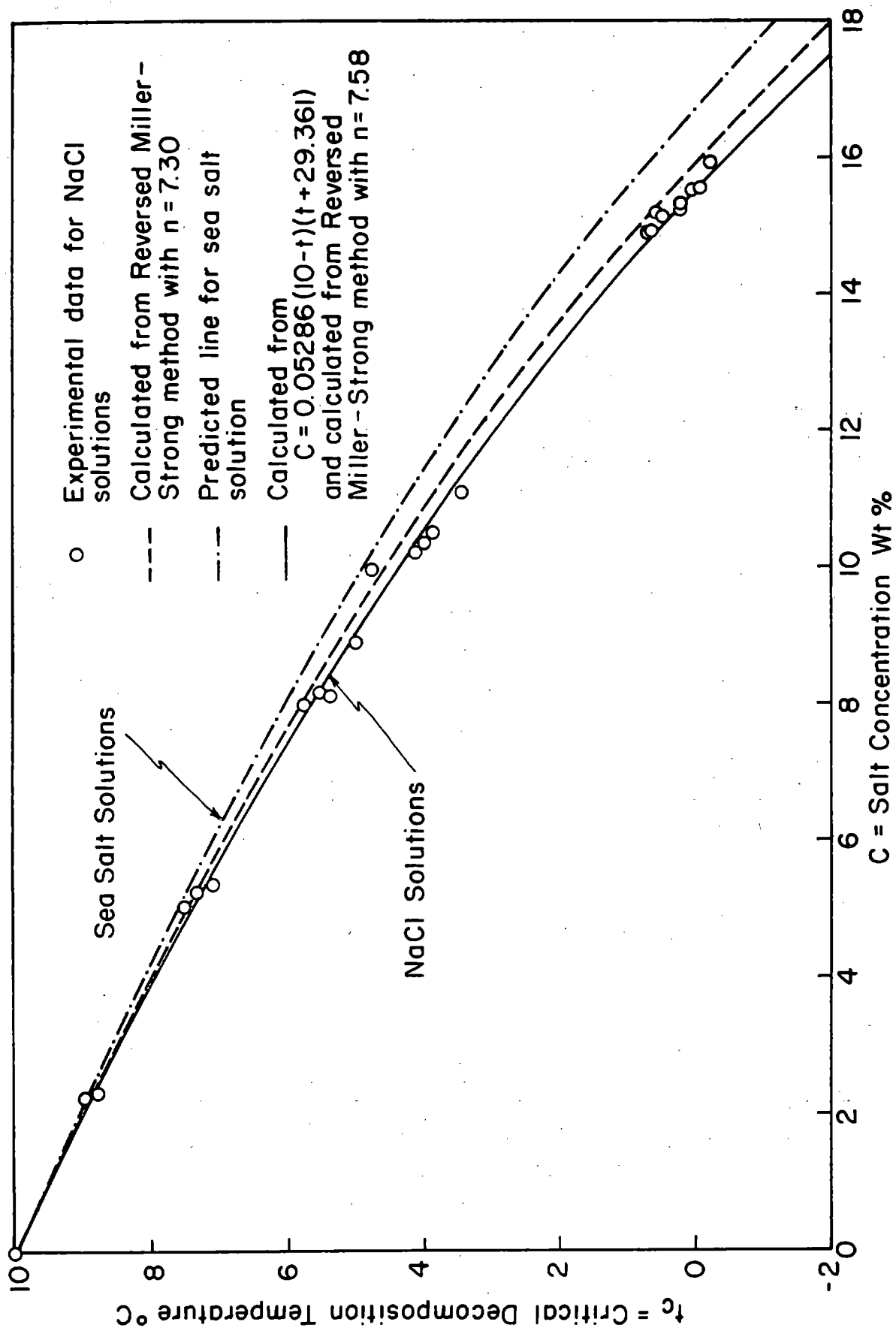


FIG. 4 SALT EFFECT ON CRITICAL DECOMPOSITION TEMPERATURE OF CO₂ HYDRATE

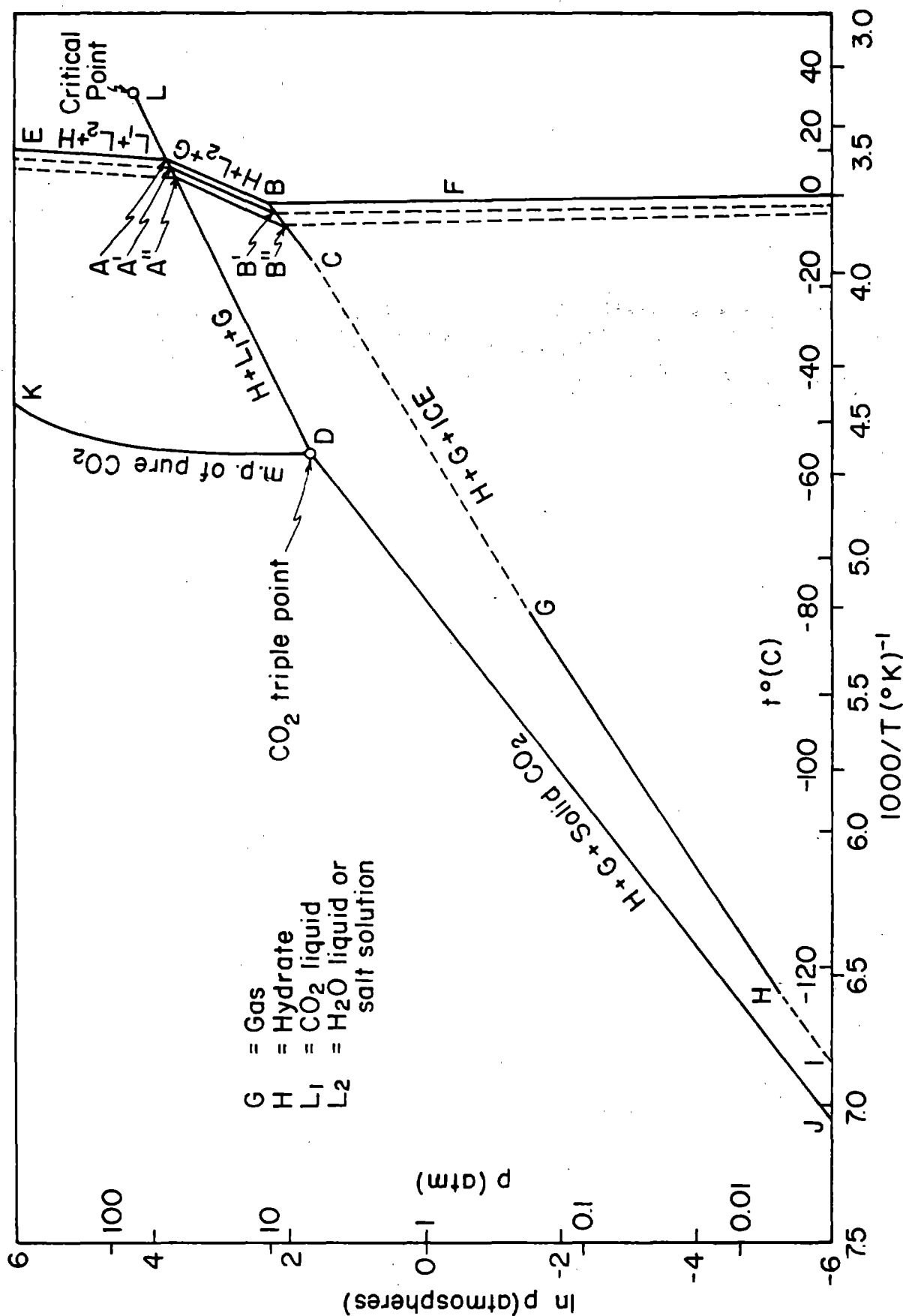


FIG.5 COMPLETE KNOWN PHASE DIAGRAM OF CO₂ HYDRATE

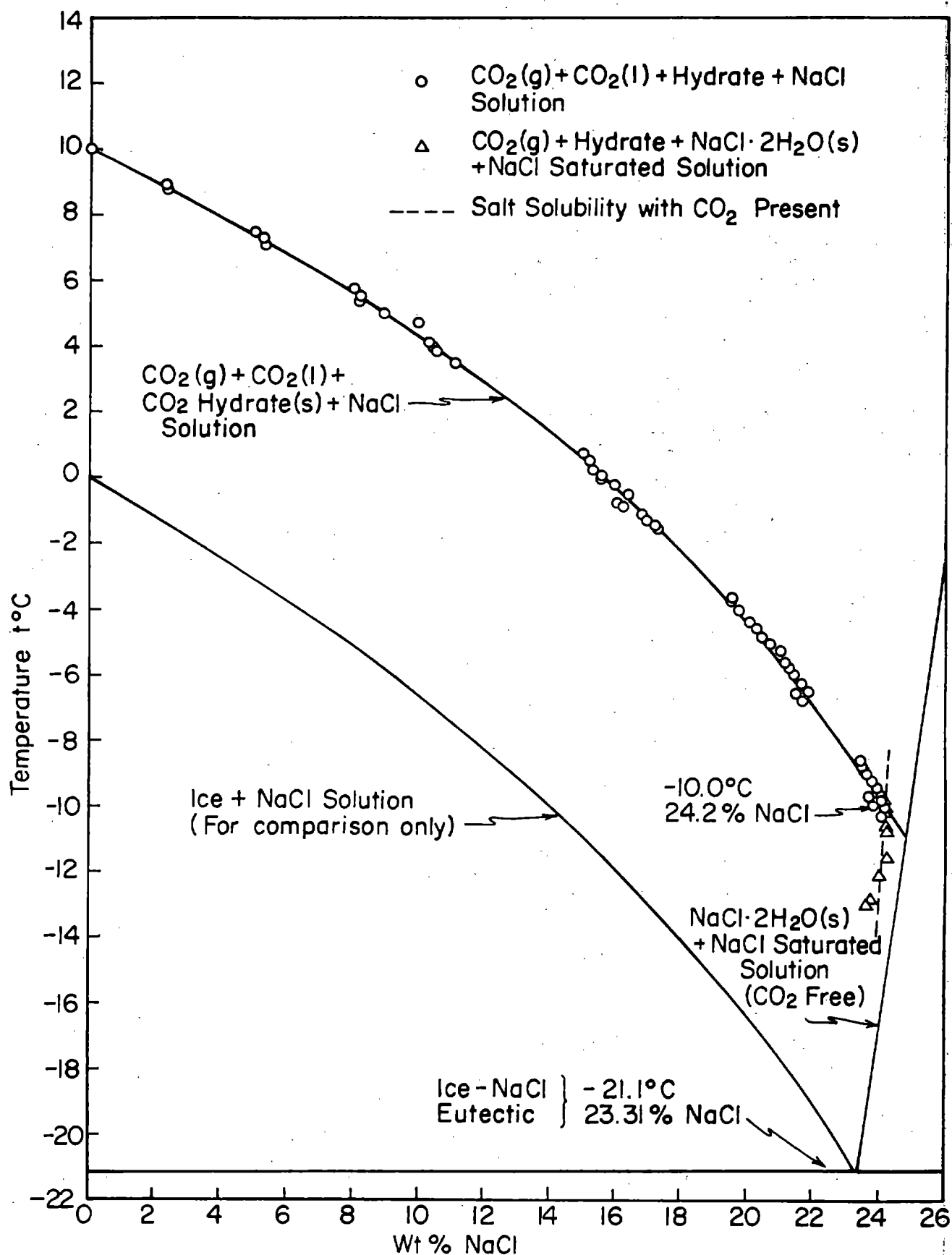
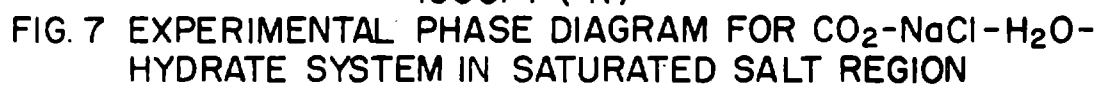


FIG. 6 SALT EFFECT ON CRITICAL DECOMPOSITION TEMPERATURE (MELTING POINT) OF CO_2 HYDRATE (LOW TEMPERATURE TO EUTECTIC)



APPENDICES

APPENDIX I

Solubility of CO₂ in Water and NaCl Aqueous Solution

The solubility data of CO₂ in water used in this work are taken from Houghton, McLean and Ritchie (R-14) and Zelvenski (R-40), and are converted into the same units of gm-CO₂/1000 g-H₂O. From the plot of solubility vs t°C with pressure as a parameter, one can interpolate the solubility data for temperatures from -1°C to 10°C. Then, these values are again plotted in (solubility/pressure) vs pressure by considering t as the parameter. At high pressure, the curve for every temperature is a straight line. It is easy to extrapolate outside the range reported, i.e. pressure from 0 to 36 atm. The solubility data for CO₂ in water along the CO₂-H₂O-hydrate line are given in Table 12.

TABLE 12 - Solubility of CO₂ in Water for CO₂-H₂O-Hydrate system

Temp.°C	-1.48	-1	0	1	2	3	4	5
Pressure (atm)	10.28	10.85	12.15	13.62	15.29	17.2	19.41	21.98
x _{CO₂} · 10 ³	13.47	13.99	14.92	15.78	16.59	17.45	18.43	19.23

Temp.°C	6	7	8	9	10
Pressure (atm)	25.00	28.58	32.86	37.77	44.40
x _{CO₂} · 10 ³	20.25	20.9	21.9	22.34	22.55

There are no solubility data for CO₂ in NaCl aqueous solution within the hydrate range. The only data obtained are measured by Munjal and Stewart (R-30) for the solubility of CO₂ in synthetic sea water and its concentrates at - 5°C to 25°C and 10 to 25 atm pressure. They also reported a correlation equation for the solubility of carbon dioxide in water, sea water, and sea water concentrates (R-20). Although they reported that the equation reproduced the experimental results within deviations of a few tenths of 1% and at the worst 0.5%, it is found that the equation always has a deviation of 2 to 8% compared with the data they presented in (R-30). This equation is not suitable to be used in this work. Because the data they reported are so few, the solubility of CO₂ in NaCl solution for a given pressure, temperature and concentration is not possible to obtain within the desired accuracy, even if we can assume that the solubility of CO₂ in NaCl solution is the same as that in sea water. Therefore, the calculation of the hydrate composition, the solubility effects are neglected.

APPENDIX II

Activity of Water in NaCl Aqueous Solution

The activity of water in NaCl solution without any hydrating agent present can be found in Bozzo's thesis (R-5). The data are listed in Table 13. These data at each temperature can be expressed by the following equation by using the least squares method:

$$-\ln a_{25^\circ\text{C}}^* = 0.00579982906W + 3.46510946 \cdot 10^{-5}W^2 + 5.652143122 \cdot 10^{-6}W^3 \quad (43)$$

and

$$-\ln a_{0^\circ\text{C}}^* = 0.005517281366W + 3.798635897 \cdot 10^{-5}W^2 + 5.148437837 \cdot 10^{-6}W^3 \quad (44)$$

where $a_{25^\circ\text{C}}^*$ and $a_{0^\circ\text{C}}^*$ are the activities of water at 25°C and 0°C , respectively, and W is the NaCl concentration expressed in weight percentage salt.

The activity at a temperature between 25°C and the freezing point, can be obtained from the above two equations by linear interpolation since the activity change with temperature is very slight.

$$\begin{aligned} -\ln a^* &= (5.517281366 + 0.0113019t) \cdot 10^{-5}W^2 \\ &+ (3.798635897 - 0.0133410575t) \cdot 10^{-5}W^2 \\ &+ (5.148437837 + 0.201482114t) \cdot 10^{-6}W^3 \end{aligned} \quad (45)$$

where a^* is the activity of water in NaCl solution at $t^\circ\text{C}$.

APPENDIX III

Thermodynamic Properties of CO_2

The equation of state of gaseous carbon dioxide used in this work was proposed by van Huff, Houghton and Coull (R-34) in 1963. The volume explicit equation of state fits the reported P-V-T data of Michels and Michels, MacCormack and Schneider, and Kennedy with an average deviation of 0.09% and a maximum of 0.5% over the range 0° to 40°C and 0 to 150 atm. The equation has been used outside the temperature range from -1.5°C to 0°C .

The equation of state is as follows:

$$PV = RT + B_1P + B_2P^2 + B_3P^3 + B_4P^4 + B_5P^5 \quad (46)$$

where

$$\begin{aligned} B_1 &= 6.4598581 \times 10^{-2} - \frac{3.394785 \times 10^1}{T} - \frac{9.6373571 \times 10^3}{T^2} + \frac{2.3793882 \times 10^6}{T^3} \\ &\quad - \frac{2.9294047 \times 10^8}{T^4} - \frac{4.8297663 \times 10^{10}}{T^5} \end{aligned}$$

TABLE 13 - Activity of Water in Salt Solution Versus Temperature (R-5)

Wt.% Salt	Freezing Point (°C)	Activity at Freezing Point	Activity at 25% from (R-25)	Interpolated Activity at 0°C
0	0.00	1.0000	1.0000	1.0000
1	- 0.58	0.9943	0.9942	0.9943
2	- 1.13	0.9891	0.9882	0.9891
3	- 1.72	0.9832	0.9823	0.9832
4	- 2.35	0.9775	0.9763	0.9774
5	- 2.97	0.9716	0.9700	0.9714
6	- 3.63	0.9652	0.9632	0.9649
7	- 4.32	0.9589	0.9565	0.9585
8	- 5.03	0.9525	0.9500	0.9521
9	- 5.77	0.9454	0.9426	0.9449
10	- 6.54	0.9384	0.9352	0.9377
11	- 7.34	0.9312	0.9272	0.9303
12	- 8.17	0.9236	0.9191	0.9225
13	- 9.03	0.9158	0.9106	0.9141
14	- 9.94	0.9076	0.9017	0.9059
15	-10.88	0.8993	0.8925	0.8972
16	-11.90	0.8907	0.8825	0.8881

Activities at the freezing point were calculated from vapor pressures and freezing points reported in the Handbook of Chemistry and Physics (R-11).

$$B_2 = 8.4227950 \times 10^{-4} - \frac{3.9977877 \times 10^{-1}}{T} - \frac{6.4659619 \times 10^1}{T^2} + \frac{3.3303766 \times 10^4}{T^4} + \frac{9.81162 \times 10^4}{T^4} - \frac{7.8247914 \times 10^8}{T^5}$$

$$B_3 = -1.657976 \times 10^{-4} + 8.214250 \times 10^{-7} T - 9.375000 \times 10^{-10} T^2$$

$$B_4 = -5.240453 \times 10^{-5} + 4.6744 \times 10^{-7} T - 1.387687 \times 10^{-9} T^2 + 1.3700 \times 10^{-12} T^3$$

$$B_5 = -1.201731 \times 10^{-7} + 7.68906 \times 10^{-10} T - 1.23125 \times 10^{-12} T^2$$

The units of P, V and T are atm, liter and °K, respectively.

From the equation of state the compressibility factors are calculated from the relationship,

$$Z = \frac{PV}{RT} = 1 + \frac{B_1}{RT} P + \frac{B_2}{RT} P^2 + \frac{B_3}{RT} P^3 + \frac{B_4}{RT} P^4 + \frac{B_5}{RT} P^5 \quad (47)$$

The fugacity can be obtained directly from the definition of fugacity coefficients (R-24).

$$\ln \frac{f}{P} = \int_0^P \frac{(Z-1)}{P} dP \quad (48)$$

The resulting definite integral is integrated term by term to obtain the following expression:

$$f = P \exp \left[(B_1 P + \frac{B_2}{2} P^2 + \frac{B_3}{3} P^3 + \frac{B_4}{4} P^4 + \frac{B_5}{5} P^5) / RT \right] \quad (49)$$

where B_i 's are functions of temperature only. These functions are expressed in Equation (46).

ΔH_{comp} can be calculated by using the definition [see Equation (16)],

$$\Delta H_{\text{comp}} = \int_0^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \quad (50)$$

By substituting the equation of state into the above equation, ΔH_{comp} can be expressed by

$$\Delta H_{\text{comp}} = C_1 P + C_2 P^2 + C_3 P^3 + C_4 P^4 + C_5 P^5 \quad (51)$$

where the relation between C_i and B_i are,

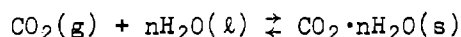
$$C_i = \frac{B_i - T \frac{dB_i}{dT}}{i} \quad i=1, \dots, 5 \quad (52)$$

APPENDIX IV

Sample Calculations

A. Composition of CO₂ Hydrate by de Forcrand's Method

For the equilibrium



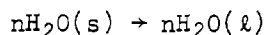
The standard heats of reaction ΔH_1° are given in Table 8. At the invariant point with ice

$$\Delta H_1^\circ = - 14.247 \text{ Kcal/g-mole}$$

For the equilibrium $\text{CO}_2(\text{g}) + n\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CO}_2 \cdot n\text{H}_2\text{O}(\text{s})$, the standard heat of reaction at the invariant point with ice has been calculated previously.

$$\Delta H_2^\circ = - 5.724 \text{ Kcal/g-mole}$$

By subtracting the two reactions, we obtain



The heat of reaction is equal to $n \cdot \Delta H_{\text{fusion}}$

$$n \cdot \Delta H_{\text{fusion}} = \Delta H_2^\circ - \Delta H_1^\circ$$

Since ΔH_{fusion} of ice is taken to be 1.437 Kcal/g-mole, the n can be easily calculated.

$$n = \frac{\Delta H_2^\circ - \Delta H_1^\circ}{1.437} = 5.93$$

B. Composition of CO₂ Hydrate by Miller-Strong's Method

As shown previously, the composition of the hydrate by using the Miller-Strong's method can be expressed by,

$$n = \frac{\ln f_2 / f_1}{\ln \left[(1-x_{\text{CO}_2,1}) / a_2^* (1-x_{\text{CO}_2,2}) \right]} \quad (53)$$

where

f = the fugacity of the gaseous phase

x_{CO_2} = the mole fraction of CO_2 in liquid phases

subscript 1 = salt free system

subscript 2 = salt solution system

Since sufficient information on the solubility of CO_2 in salt solution is not available and $x_{\text{CO}_2,2}$ in practice tends to be equal to $x_{\text{CO}_2,1}$, Equation (53) can be expressed

$$n = \frac{\ln f_2 / f_1}{-\ln a_2^*} \quad (54)$$

by neglecting the corrections on activity due to dissolved CO_2 .

Equilibrium point No. 25 reported in Table 4 shall be used for this sample calculation. The equilibrium pressure and temperature determined experimentally are 303.8 psia (20.672 atm) and 0.01°C , respectively. The reactor sample is taken to determine the concentration of NaCl . The result of the analysis is 10.30 wt.% NaCl .

Using the experimental data the procedures of the application of the Miller-Strong's method are as follows. At first the pressure along the pure water hydrate line at the experimental temperature 0.01°C has to be found. It can be calculated from Equation (28).

$$\ln P(\text{atm}) = -58105.56177 + 8185.485312 \ln T + \frac{4,430,531.757}{T} - \frac{300,893.013}{T^2(^{\circ}\text{K})} \quad (28)$$

Thus, the pressure along the pure water hydrate line is 12.165 atm.

These pressures are converted into fugacities by using Equation (49). The fugacity for the pure water hydrate line is,

$$f_1 = 11.157 \text{ atm}$$

The fugacity for the NaCl solution-hydrate line is,

$$f_2 = 17.795 \text{ atm}$$

Activities for the water- NaCl system are presented in Appendix II. Using the experimental temperature 0.01°C and the concentration 10.3% NaCl , the activity of water a_2^* can be easily calculated from Equation (45).

$$a_2^* = 0.93568$$

Then, the composition of carbon dioxide hydrate can be calculated from Equation (54).

$$n = \frac{\ln 17.795/11.157}{- \ln 0.93568} = 7.02 \quad (55)$$

A detailed summary of the calculation of the CO₂ hydrate composition by the Miller-Strong method for all the experimental data, is tabulated in Table 14.

TABLE 14 - Composition of Carbon Dioxide Hydrate by the Miller-Strong Method

No.	Temp. °C	Wt.% Salt(CO ₂ Free)	P ₂ atm	f ₂ atm	f ₁ atm	a ₂ [*]	lnf ₂ /f ₁	- ln a ₂ [*]	n
1	2.974	5.42	22.67	19.34	15.23	0.9684	0.2390	0.03211	7.44
2	4.017	5.28	25.62	21.43	17.02	0.9692	0.2302	0.03129	7.36
3	6.00	5.3	33.27	26.38	21.10	0.9689	0.2231	0.03159	7.06
4	6.42	4.865	34.23	29.97	22.10	0.9716	0.1992	0.02882	6.91
5	6.843	5.37	38.26	29.23	23.15	0.9684	0.2329	0.03212	7.25
6	2.723	5.27	21.30	18.35	14.83	0.9694	0.2127	0.03112	6.84
7	3.235	5.72	23.02	19.60	15.66	0.9665	0.2245	0.03408	6.59
8	3.847	5.76	25.01	21.00	16.71	0.9662	0.2285	0.03441	6.64
9	4.348	5.80	27.59	22.75	17.64	0.9659	0.2545	0.03472	7.33
10	4.779	5.545	28.48	23.35	18.48	0.9675	0.2342	0.03308	7.08
11	5.48	5.445	31.89	25.52	19.94	0.9680	0.2467	0.03249	7.59
12	6.18	5.45	34.83	27.29	21.52	0.9679	0.2374	0.03259	7.29
13	6.552	5.53	36.79	28.41	22.42	0.9674	0.2366	0.03315	7.14
14	-1.545	4.79	13.02	11.84	9.48	0.9726	0.2229	0.02775	8.03
15	-1.06	5.215	13.8	12.49	9.97	0.9700	0.2249	0.03045	7.39
16	-0.56	5.375	14.82	13.32	10.51	0.9690	0.2368	0.03150	7.52
17	-0.02	5.26	15.69	14.02	11.12	0.9697	0.2313	0.03082	7.51
18	0.50	5.385	16.87	14.96	11.74	0.9688	0.2418	0.03166	7.64
19	0.915	4.665	17.14	15.18	12.27	0.9732	0.2130	0.02715	7.85
20	1.50	5.715	19.02	16.62	13.04	0.9667	0.2429	0.03388	7.17

(Continued)

TABLE 14 (Cont'd.)

No.	Temp. °C	Wt. % Salt(CO ₂ Free)	P ₂ atm	f ₂ atm	f ₁ atm	a ₂ [*]	ln f ₂ /f ₁	- ln a ₂ [*]	n
21	2.13	4.81	19.92	17.31	13.93	0.9723	0.2173	0.02815	7.72
22	7.213	5.875	41.71	31.00	24.12	0.9651	0.2508	0.03551	7.06
23	-1.535	10.17	17.12	15.10	9.49	0.9371	0.4648	0.06498	7.15
24	-0.53	10.33	19.98	17.27	10.54	0.9356	0.4934	0.06655	7.41
25	0.01	10.30	20.67	17.80	11.16	0.9357	0.4668	0.06649	7.02
26	1.015	10.31	23.52	19.85	12.39	0.9353	0.4711	0.06689	7.04
27	1.54	10.50	26.16	21.66	13.09	0.9337	0.5032	0.06860	7.34
28	2.02	10.30	27.50	22.55	13.77	0.9351	0.4933	0.06714	7.35
29	2.533	10.46	30.00	24.15	14.54	0.9337	0.5078	0.06861	7.40
30	3.004	10.26	31.44	25.05	15.28	0.9351	0.4946	0.06713	7.37
31	3.565	10.37	33.89	26.52	16.22	0.9341	0.4917	0.06821	7.21
32	4.027	10.27	35.72	27.57	17.04	0.9347	0.4813	0.06754	7.13
33	4.227	10.21	37.17	28.37	17.41	0.9351	0.4882	0.06711	7.28
38	-0.967	10.25	18.94	16.49	10.07	0.9363	0.4932	0.06578	7.50
39	0.52	10.22	22.31	18.99	11.77	0.9361	0.4783	0.06602	7.24
40	1.37	10.20	24.55	20.57	12.86	0.9360	0.4696	0.06612	7.10
41	2.152	10.32	28.55	23.23	13.96	0.9349	0.5088	0.06734	7.56
42	2.222	10.30	28.40	23.14	14.07	0.9350	0.4978	0.0672	7.41
43	3.164	10.19	31.91	25.34	15.54	0.9356	0.4891	0.06661	7.34
44	3.345	10.29	32.89	25.93	15.84	0.9348	0.4929	0.06748	7.30
45	3.776	10.16	34.09	26.65	16.59	0.9356	0.4743	0.06656	7.13

(Continued)

TABLE 14 (Cont'd.)

No.	Temp. °C	Wt. % Salt(CO ₂ Free)	P ₂ atm	f ₂ atm	f ₁ atm	a ₂ [*]	lnf ₂ /f ₁	- ln a ₂ [*]	n
46	3.796	10.41	35.21	27.27	16.62	0.9337	0.4951	0.06861	7.22
47	4.047	10.20	36.33	27.90	17.08	0.9352	0.4911	0.06697	7.33
48	0.03	5.871	16.32	14.52	11.18	0.9659	0.2610	0.03475	7.51
49	1.035	5.917	18.41	16.15	12.42	0.9655	0.2625	0.03515	7.47
50	1.921	5.834	20.29	17.58	13.63	0.9659	0.2548	0.03470	7.34
51	3.025	5.764	23.24	19.74	15.31	0.9662	0.2541	0.03435	7.40
52	3.455	6.132	25.21	21.12	16.03	0.9638	0.2760	0.03683	7.49
53	3.998	5.733	26.40	21.95	16.99	0.9663	0.2564	0.03424	7.49
54	4.578	5.860	28.61	23.43	18.08	0.9655	0.2591	0.03514	7.37
55	5.06	5.949	30.31	24.53	19.05	0.9649	0.2529	0.03578	7.07
56	5.53	5.632	31.80	25.47	20.05	0.9668	0.2393	0.03373	7.10
57	6.01	5.568	33.93	26.77	21.13	0.9672	0.2366	0.03335	7.09

A REVIEW OF THE PROPERTIES OF GAS HYDRATES

M. Suwandi

The following tables list many of the important properties of 51 gas hydrates and the agents that form them. All hydrates listed are those formed from a single pure agent and water.

Every source of data available to us was used to make this compilation, but two of these were most useful: Office of Saline Water Research and Development Progress Reports (7-10, 12, 13, 17, 19, 38, 47, 63), and Stackelberg's review covering a period starting in the early nineteenth century (69). du Pont Technical Bulletins (30-37) were useful for finding properties of many hydrate forming agents. Other reviews on the nature and properties of these gas hydrates are those of Byk and Fomina (15), Kase (46), Hagan (43), and Bhatnagar (11). Because of its economic interest in the desalination processes, Barduhn (25) et al have studied the rate of hydrolysis of some hydrate forming substances, although such data are not included in the tables.

The amount of information on hydrates varies markedly from one substance to the other, and we have thus divided them into two major tables. Table I consists of substances which, in general, one can find extensive information, and Table II is concerned with hydrates about which the information was very limited. In many cases, the P-T (pressure-temperature) phase equilibrium data were obtained only at one or two points, e.g. at 0°C and at 1 atm. Each value given in these two tables is followed by one or more numbers in parentheses or brackets which indicate the corresponding reference. If there is more than one reference, then the information given corresponds to the first reference. The other references provide the same information but, sometimes, with considerably different values, i.e. we have made a value judgement of the data quality.

The listing of the substances in each table was according to the following order: First, the hydrocarbons, followed by the halocarbons, and finally, by the "permanent" gases. The hydrocarbons are arranged according to the number of C atoms first and then H atoms. The isomers (if any) come after the normal molecules. The halocarbons were arranged according to their "refrigerant" numbers, a nomenclature used by all the major manufacturers of these compounds and started by du Pont who call them "Freons", a trade marked name. The system can be described as follows:

Each molecular formula (when no bromine is present) is assigned a four digit number:

WXYZ

where

W = 0 if the molecule contains only single bonds

W = 1 if the molecule contains a double bond

W = 2 if the molecule contains a triple bond

X = one less than the number of carbon atoms in the molecule

Y = one more than the number of hydrogen atoms in the molecule

Z = the number of fluorine atoms in the molecule

Additional rules are:

1. The number of chlorine atoms is determined by difference.
2. Initial zeros are understood and not written, e.g., CCl_2F_2 is Refrigerant-12 and not 0012, and hexachloroethane is Refrigerant-110, not 0110.
3. When bromine is present the suffix Bn is added where n is the number of bromine atoms per molecule; thus methyl bromide is Refrigerant-40B1.
4. Cyclic compounds have the prefix C. Thus, perfluoro cyclobutane has the number C318.
5. When more than one structural isomer is possible in the ethane or ethylene series, that isomer which is most symmetrical is numbered according to the rules above. Other isomers are given a small letter suffix with "a" indicating the second most symmetrical and "b" the third, etc. The degree of symmetry is determined by comparing the sums of the atomic weights of the atoms attached to each carbon atom. Thus:
 $\text{CHF}_2 - \text{CHFC}\ell = \text{Refrigerant 133}$ (39 vs 55 wt. units attached to C's)
 $\text{CH}_2\text{C}\ell - \text{CF}_3 = \text{Refrigerant 133a}$ (37 vs 57)
 $\text{CH}_2\text{F} - \text{CF}_2\text{C}\ell = \text{Refrigerant 133b}$ (21 vs 73)
 This suffix is written after the bromine suffix.
6. No distinction is made among optical, cis-trans, or iso-normal isomers.
7. The system can be used for only a limited number of compound containing more than two carbon atoms.

Molecules containing iodine are listed after the same molecules where the iodine atom has been substituted by bromine, e.g., CH_3I listed after CH_3Br . Finally, the "fixed" gases were arranged in alphabetical order.

The properties listed in these tables are the physical properties of the hydrate forming materials, such as normal boiling point, liquid density, solubility in water, etc., and the properties of their hydrates: hydrate composition, crystal structures, crystal densities, lower and upper invariant points, P-T phase equilibrium data and their relationships, heats of formation, depression of upper invariant point in the presence of salts. The upper invariant point (called also critical decomposition temperature and pressure) is defined as the temperature and pressure at which exist four phases: aqueous liquid (W), agent liquid (L), gas (G), and the solid hydrate (H), and, therefore, the degree of freedom is zero. The lower invariant point (called also invariant point with ice) is another state with zero degrees of freedom and involves aqueous liquid (W), ice (I), gas (G), and hydrate (H).

The hydrate compositions listed in these tables are mostly determined by direct analysis, but those with the square brackets were estimated by thermodynamic methods described by Barduhn (9,13) (5,9) or estimated from their lattice constant obtained from a study of their x-ray powder pattern. The direct analysis is likely to be inaccurate because of the difficulty of obtaining dry crystals uncontaminated with adhering liquid, although one method circumvents this problem. The indirect methods are:

1. x-ray powder pattern
2. Miller and Strong method
3. Method of de Forcrand

From x-ray studies, one may determine lattice constants and the number of water molecules and cages in a unit cell. This yields hydrate numbers (n) of $5\frac{3}{4}$, $7\frac{2}{3}$, or 17 moles of water per mole of agent, but these three numbers are only lower limits to n since all of the cages need not be filled with the guest molecules. Actual values of n may be as much as 25% greater than the theoretical values indicating only 80% of occupancy of the cages. The hydrate number often decreases with increasing temperature and pressure (greater degree of occupancy). For a few hydrates, n is less than the theoretical value indicating greater than 100% occupancy of the cages by the agent molecules. This can mean either a deficiency in the assumed model of the unit cell or an inaccurate determination of n . Examples of this dilemma are the hydrates of argon, R-12, and R-13B1.

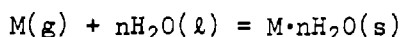
According to the method of Miller and Strong, the composition is determined from the following relation:

$$n = \frac{\log f_2/f_1}{\log a_1/a_2} \quad (1)$$

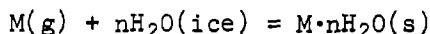
where f_1 and f_2 are the fugacities of the agent gas in the vapor phase above pure water and salt solution but at the same temperature, respectively; and a_1 and a_2 are, respectively, the activity of water in pure water and in salt solution. The pure water may not have an activity of 1 since it may contain some dissolved gaseous agent. The method of de Forcrand utilizes the following formula:

$$n = \frac{\Delta H_1 - \Delta H_2}{1437} \quad (2)$$

where ΔH_1 and ΔH_2 are the heat of reactions, in cal/g.mole, of the following reactions:



and



The heat of fusion of ice is the difference between these two equations and = 1437 cal/g.mole.

Barduhn (9,13) described a method of calculating the hydrate crystal density from its molecular weight, hydrate composition, and its lattice constant. It is determined from the following equations for ρ in gms/cm³.

For Structure I:

$$\rho_I = 0.797 \left(1 + \frac{MW}{18n} \right) \left(\frac{12.00}{\text{lattice constant}} \right)^3 \quad (3)$$

For Structure II:

$$\rho_{II} = 0.787(1 + \frac{MW}{18n})(\frac{17.30}{\text{lattice constant}})^3 \quad (4)$$

The calculated crystal density is given in column 8 of the two tables. If there is no lattice constant written in column 7, then the crystal density was determined from Equations (3) or (4), assuming the lattice constant was 12 Å or 17.3 Å, depending on the crystal structure. If a reference number is given, then the crystal density was calculated earlier in this reference.

Some of the solubilities (S) and heat of solutions listed in columns 4 and 5 of these two tables were calculated according to a method described by Glew and Moelwyn-Hughes (41). They were calculated from the following equations:

$$\Delta H(\frac{\text{cal.}}{\text{g.mole}}) = \Delta H^\circ + T\Delta C_p \quad (5)$$

$$S(\text{in.wt.\%}) \approx \frac{PM/10}{\text{antilog}_{10}(a-b \log_{10} T-c/T)} \quad (6)$$

where

P = pressure in mm Hg

M = molecular weight of agent (7)

c = $\Delta H^\circ / (2.303R)$

$$b = - \Delta C_p / R \quad (8)$$

where ΔH is the heat of solution, ΔH° is the heat of solution extrapolated to zero absolute temperature, ΔC_p is equal to $C_p(\text{gas}) - C_p(\text{aqueous})$, which is equal to $-bR$, S is solubility of the gas in water (wt.%), and a, b and c are constants, determined experimentally from solubility measurements at several temperatures and pressures. Equation (6) assumes the solution density to be 1 gm/cc, which is reasonable, since the gases are sparingly soluble. The term in parenthesis in Equation (6) is the antilogarithm of the Henry's law constant in mm l/g.mole. Glew (41) lists the values of ΔH° , ΔC_p , and the constant a, so that the estimation of solubilities of several gases was made possible.

Solubilities tabulated by Stephen and Stephen (70) sometimes were given at several temperatures and pressures, and if we assume relations (5), (6), (7) and (8) are also applicable, then the solubility and ΔH can be calculated at any desired temperature and pressure.

P-T phase equilibrium relation can frequently be represented by equation

$$\ln P = A - \frac{B}{T} \quad (9)$$

If this be the case, the values of A and B are given in column 11 of Table I or column 12 of Table II, and the "uncorrected heat of reaction" was calculated from

$$\Delta H = 4.57 BZ \quad (10)$$

where Z is the compressibility factor of the gas. Otherwise, only the references are given. The values thus obtained are not exact because of the approximations implicit in the Clausius-Clapeyron equation. Corrections may be made for gas solubility in water, water vapor in the gas, and for the volumes of the solid and liquid phases all of which are assumed 0 in Equation 10. Together these correction factors usually amount to only a few percent and to some extent they cancel each other. Some of the heats of reaction given in the tables have been corrected, and they are identified by subscripts C. In the case of CO₂ hydrate the corrections are substantial because of the high pressure.

In the last columns are listed the references for additional sources of information that may be of interest. A brief explanation of pertinent information available in each reference is also given.

TABLES I AND II

These two tables are large and cannot be put on a single page. Table I has 15 columns and 24 lines, while Table II has 14 columns and 27 lines. To eliminate the need for a cumbersome foldout or for reducing the size excessively, they have been typed in sections and are to read as if they were assembled according to the following diagram. The page numbers are shown in the appropriate position. The headings and column 1 are repeated where appropriate so that the tables can be used in place if desired without assembling.

TABLE I

62	65	68	71
63	66	69	72
64	67	70	73

TABLE II

74	77	80
75	78	81
76	79	82

See the test for an explanation of the symbols used.

TABLE I

1	2	3	4	5	6	7	8
Agent	Agent Normal Boiling Point (°C)	Agent Liquid Density at Normal B.P. or at Temp. stated (g/cm ³)	Solubility in H ₂ O at Cr. Decomp. Temp. and Press. (wt.%) or at a stated condition	Heat of Solution at Cr. Decomp. Temp. or at stated condition (cal/g-mole)	Hydrate Composition moles H ₂ O moles agent	Hydrate Crystal Structure/Lattice Constant (if any)	Calculated Crystal Density (g/cm ³)
1. Ethylene (C ₂ H ₄)	-103.7 (18)	0.567 (18)	0.139 ^g (41)	4981 ^g (41)(29)	7.0 (29)(22)	I (29)	0.964
2. Propylene (C ₃ H ₆)	-47.7 (53)	0.615 (53)	0.083 ^o (70)		17 (23)	II (23)	0.895
3. Cyclopropane (c-C ₃ H ₆)	-33 (18)	0.72 ⁻⁷⁹ (18)			8(Str.I) 17(Str.II) (42)	I & II (42)	I: 1.03 II: 0.895
4. Propane (C ₃ H ₈)	-45 (18)	0.58 (8)	0.06 (50)		17.95 (21)	II (9)	0.88 (13)
5. Iso-Butane (i-C ₄ H ₁₀)	-11.6 (18)	0.593 (63)	negligible (63)		17.5 (63)	II (63)	0.93
6. F-11 (CCl ₃ F)	23.8 (36)	1.46 (37)	1.06x10 ⁻⁵ wt.fr. psia at 2°C (14)		16.6 (14)	II (14)	1.15
7. F-12 (CCl ₂ F ₂)	-29.8 (36)	1.49 (31)			15.26 (14)	II (14)	1.13
8. F-12B1 (CClF ₂ Br)	-3.89 (36)	1.91 (8)	0.34 (7)		16.57 (12)(40)	II (13)	1.22 (13)
9. F-13B1 (CBrF ₃)	-57.8 (36)				15.6 (14)	II (8)	1.21
10. F-20 (CHCl ₃) Chloroform	61.2 (18)	1.41 (8)	4.75 (41)	11148 (41)	[17] (69)	[II] (69)	1.09

(Continued)

TABLE I (Cont'd.)

1	2	3	4	5	6	7	8
Agent	Agent Normal Boiling Point (°C)	Agent Liquid Density at Normal B.P. or at Temp. stated (g/cm ³)	Solubility in H ₂ O at Cr. Decomp. Temp. (wt.%) or at a stated condition	Heat of Solution at Cr. Decomp. Temp. or at stated condition (cal/g-mole)	Hydrate Composition moles H ₂ O moles agent	Hydrate Crystal Structure/Lattice Constant (if any)	Calculated Crystal Density (g/cm ³)
11. F-21 (CHCl ₂ F)	8.92 (36)	1.40 (32)	1.82 (7)	8430 (7)(17)	16.8 (7)(10)(6)	II (13)	1.05 (13)
12. F-22 (CHClF ₂)	- 40.8 (36)	1.27 (37)	7.08x10 ⁻⁴ wt.fr. (14) psia		12.6 (14)	I trans. (8)	1.10
13. F-30 (CH ₂ Cl ₂) Methylene Chloride	41.4 (18)	1.29 (8)	7.8 (41)	9430 (41)	[17] (69)	[II]/17.31 (69)	1.004
14. F-31 (CH ₂ ClF)	- 8.9 (36)	1.21 (8)	4.17 (7)	6244 (7)(17)	8.10 (7)(9)	I trans. (13)	1.18 (13)
15. F-32 (CH ₂ F ₂) Methylene Fluoride	- 51.6 (18)	1.15 (8)			[8]	[I trans.]	1.08
16. F-40 (CH ₃ Cl) Methyl Chloride	- 23.7 (18)	1.03 (8)	2.94 (7)	5867 (41)	7.2 (22)(41)	I trans./12.00 (13)(69)	1.11 (13)
17. F-40B1 (CH ₃ Br) Methyl Bromide	3.65 (34)(69)	1.72 (31)	2.87 (7)	6735 (7)(17)	7.89 (7)(9)	I trans./12.09 (13)(69)	1.30 (13)
18. F-142b (CH ₃ CClF ₂)	- 10 (36)	1.23 (8)	0.045 (7)	6970 (17)(47)	17.18 (12)	II (13)	1.04 (13)
19. F-152a (CH ₃ CHF ₂)	- 24.76 (35)	1.194 (35)	0.16 (33)		8.0 (7)	I trans. (13)	1.18 (13)

(Continued)

TABLE I (Cont'd.)

1	2	3	4	5	6	7	8
Agent	Agent Normal Boiling Point (°C)	Agent Liquid Density at Normal B.P. or at Temp. stated (g/cm ³)	Solubility in H ₂ O at Cr. Decomp. Temp. and Press. (wt.%) or at a stated condition	Heat of Solution at Cr. Decomp. Temp. and Press. or at stated condition (cal/g-mole)	Hydrate Composition moles H ₂ O moles agent	Hydrate Crystal Structure/Lattice Constant (if any)	Calculated Crystal Density (g/cm ³)
20. Carbon Dioxide (CO ₂)	-79 (18)	*1.01 ³⁷ (18)	6.1 (41)	4026 (41)	7.30 (19)(22)	I/12.04 (13)(69)	1.11 (19)
21. Chlorine (Cl ₂)	-34.0 (18)		2.64 (76)	21291 (41)	6.20 (38)(1)	I trans./12.03 (13)(69)	1.22 (13)
22. Hydrogen Sulfide (H ₂ S)	-60 (18)		7.3 (41)	4076 (41)	6.0 (64)(22)	I/12.00	1.05
23. Nitrogen (N ₂)	-196.8 (18)	0.8081 (18)	0.41 ² (41)	3726 ² (41)	6.01 (24)	I (24)	1.003
24. Oxygen (O ₂)	-183 (18)	1.149 (18)	0.73 ² (41)	4008 ² (41)	6.06 (24)	I (24)	1.03

(Continued)

² - superscript means evaluated at lower invariant point

* - superscript means temperature at °C

TABLE I (Cont'd.)

1	9		10		11					
	Hydrate Critical Decomposition		Invariant Point with Ice		Constants in Equation					
	Temp. (°C)	Press. (mm Hg)	Temp. (°C)	Press. (mm Hg)	Log P (mm Hg) = A - B/[t°C + 273.16]					
					M(g) + nW(l) = H		M(g) + H = M(l) + H		M(g) + nW(ice) = H	
Agent					A	B	A	B	A	B
1. Ethylene (C ₂ H ₄)			-0.1 (29)	4134.4 (29)	See Ref. (29)				See Ref. (29)	
2. Propylene (C ₃ H ₆)	0.958 (23)	4508 (23)	-0.134 (23)		See Ref. (23)				4.4853 (16)	1072 (16)
3. Cyclopropane (c-C ₃ H ₆)	17.0 (9)(42)	4470 (9)(42)	-0.05 (42)	470.2 (42)	See Ref. (42)				See Ref. (42)	
4. Propane (C ₃ H ₈)	5.7 (9)	4140 (9)				7208 (39)				1424 (39)
5. Iso-Butane (i-C ₄ H ₁₀)	1.88 (63)	1256 (63)	0 (63)	851 (63)	27.6860 (63)	6762.4 (63)	7.2878 (63)	1151.2 (63)	7.292 (63)	1192 (63)
6. F-11 (CCl ₃ F)	8.28 (20)	656.6 (20)			See Ref. (20)		See Ref. (20)			
7. F-12 (CCl ₂ F ₂)	9.9 (20)	3216 (20)			See Ref. (20)		See Ref. (20)			
8. F-12B1 (CClF ₂ Br)	9.9 (9)(40)	1272 (9)(40)	0.0 (9)(40)	147 (9)(40)	28.95234 (9)(40)	7316.6 (9)(40)	7.48253 (9)(40)	1239.3 (9)(40)	See Ref. (40)	
9. F-13B1 (CBrF ₃)	10-12 (14)				See Ref. (14)		See Ref. (14)			
10. F-20 (CHCl ₃) Chloroform	1.10 (72)(69)	67.8 (72)(69)	-0.6 (72)	49.2 (72)	See Ref. (72)		See Ref. (72)		See Ref. (72)	
11. F-21 (CHCl ₂ F)	8.69 (10)	761 (10)			29.8004 (10)(6)	7538.05 (10)(6)	7.6641 (10)(6)	1347.95 (10)(6)	See Ref. (6)	

(Continued)

TABLE I (Cont'd.)

1	9		10		11				
	Hydrate Critical Decomposition		Invariant Point with Ice		Constants in Equation				
	Temp. (°C)	Press. (mm Hg)	Temp. (°C)	Press. (mm Hg)	Log P(mm Hg) = A - B/[t°C + 273.16]				
					M(g) + nW(l) = H		M(g) + H = M(l) + H		M(g) + nW(ice) = H
Agent					A	B	A	B	A
12. F-22 (CHClF ₂)	17.5 (20)	7238 (20)			See Ref. (20)		See Ref. (20)		
13. F-30 (CH ₂ Cl ₂) Methylene Chloride	1.85 (72)(69)	166.3 (72)(69)	-0.1 (72)	121 (72)	See Ref. (72)		See Ref. (72)		See Ref. (72)
14. F-31 (CH ₂ ClF)	17.88 (9)	2147 (9)	-0.2 (9)	169 (9)	19.15611 (9)	4605.5 (9)	7.66967 (9)	1262.5 (9)	
15. F-32 (CH ₂ F ₂) Methylene Fluoride	20.4 (5)	11020 (5)	-0.074 (5)	1034 (5)	17.7 (5)	4016 (5)	7.18 (5)	921.7 (5)	
16. F-40 (CH ₃ Cl) Methyl Chloride	20.4 (7)(20)	3640 (7)(20)	-0.18 (7)	269 (7)	17.0387 (7)	3988 (7)(20)	6.9651 (7)(20)	1002 (7)(20)	8.099 (7)
17. F-40B1 (CH ₃ Br) Methyl Bromide	14.73 (9)(69)	1151 (9)(69)	-0.24 (9)	181 (9)	17.7271 (9)	4222.22 (9)	7.5659 (9)	1296.84 (9)	8.6676 (9)
18. F-142b (CH ₃ CClF ₂)	13.09 (9)	1743 (9)	-0.04 (9)	103.4 (9)	28.7854 (9)	7311.8 (9)	7.33942 (9)	1173.0 (9)	8.00995 (9)
19. F-152a (C ₂ H ₄ F ₂)	14.9 (9)	3270 (9)	0.0 (9)	410 (9)	20.1126 (9)	4781 (9)	7.6162 (9)	1181 (9)	9.243 (9)
20. Carbon Dioxide (CO ₂)	10.00 (19)	33744 (19)	-1.48 (19)	7795 (19)	(19)**	(19)	7.4125 (19)	856.01 (19)	8.7476 (19)
21. Chlorine (Cl ₂)	28.3 (47)	6390 (47)	-0.24 (61)	244 (61)	17.783 (47)	4213.7 (47)	7.2796 (47)	1047.3 (47)	7.6231 (47)

(Continued)

TABLE I (Cont'd.)

1	9		10		11					
	Hydrate Critical Decomposition		Invariant Point with Ice		Constants in Equation					
	Temp. (°C)	Press. (mm Hg)	Temp. (°C)	Press. (mm Hg)	Log P(mm Hg) = A - B/[t°C + 273.16]			M(g) + nW(lce)		
					M(g) + H =			M(g) + nW(lce) = H		
Agent					A	B		A	B	
22. Hydrogen Sulfide (H ₂ S)	29.6 (64)	16720 (64)	-0.389 (64)	697 (64)	17.992 (66)	6867.98 (66)	8.4547 (66)	1668.63 (66)	7.7373 (64)	1332 (64)
23. Nitrogen (N ₂)			-1.3 (24)	107540 (24)	17.0101 (24)	3257 (24)			8.4406 (24)	927 (24)
24. Oxygen (O ₂)			-1.0 (24)	82992 (24)	17.189 (24)	3340 (24)			7.9976 (24)	838 (24)

**Four constant equations:

(Continued)

$$\log P(\text{mm Hg}) = -25232.043 + 1543.88 \log T + \frac{1924155.5}{T} - \frac{130676175}{T^2}$$

TABLE I (Continued)

1	Agent	12 Compressibility of M(g) at Critical De- composition Temperature and Pressure Z	13 Uncorrected Heat of Reaction		
			M(g) + nW(l) = H ($\frac{\text{kcal}}{\text{g-mole}}$)	M(g) + H = M(l) + H ($\frac{\text{kcal}}{\text{g-mole}}$)	M(l) + nW(l) = H ($\frac{\text{Btu}}{\text{lb.H}_2\text{O}}$)
12.	F-22 (CHClF ₂)	0.855	25.099 _c (14)	6.998 _c (14)	
13.	F-30 (CH ₂ Cl ₂) Methylene Chloride				
14.	F-31 (CH ₂ ClF)	0.935 (9)	18.530 _c (9)	5.399 (9)	162 _c (7)
15.	F-32 (CH ₂ F ₂) Methylene Fluoride				
16.	F-40 (CH ₃ Cl) Methyl Chloride	0.918 (7)	16.75 (7)	4.21 (7)	157 (7)
17.	F-40B1 (CH ₃ Br) Methyl Bromide	0.967 (9)	18.45 _c (9)(69)	5.74 (9)	162 _c (7)
18.	F-142b (CH ₃ CClF ₂)	0.930 (12)	31.11 (12)	4.99 (12)	152 (12)
19.	F-152a (CH ₃ CHF ₂)	0.900 (7)	19.68 (7)	4.86 (7)	185 (7)
20.	Carbon Dioxide (CO ₂)	0.625 (19)	13.16 (19)	2.07 (19)	152 (19)
21.	Chlorine (Cl ₂)	0.8966 (38)	19.2739 (47)	4.3099 (47)	167 (47)
22.	Hydrogen Sulfide (H ₂ S)				

(Continued)

TABLE I (Cont'd.)

1	Agent	12 Compressibility of M(g) at Critical De- composition Temperature and Pressure Z	13 Uncorrected Heat of Reaction			
			M(g) + nw(l) = H ($\frac{\text{kcal}}{\text{g-mole}}$)	M(g) + H = M(l) + H ($\frac{\text{kcal}}{\text{g-mole}}$)	M(l) + nw(ice) = H ($\frac{\text{kcal}}{\text{g-mole}}$)	M(l) + nw(l) = H ($\frac{\text{Btu}}{\text{lb.H}_2\text{O}}$)
1.	Ethylene (C ₂ H ₄)	0.958 (29)	14.870 ^l (29) ^c		5.255 ^l (29) ^c	
2.	Propylene (C ₃ H ₆)					
3.	Cyclopropane (c-C ₃ H ₆)		Str. I: 19.06 ^c II: 29.2 ^c (42)		Str. I: 7.405 ^c II: 6.424 ^c (42)	
4.	Propane (C ₃ H ₈)	≈ 1 (39)	32.103 (39)		6.343 (39)	150 (39)
5.	Iso-Butane (i-C ₄ H ₁₀)	0.937 (63)	28.9 ^c (63)			146 (63)
6.	F-11 (CCl ₃ F)		35.447 (14)		11.571 (14)	
7.	F-12 (CCl ₂ F ₂)		30.114 ^c (14)		7.793 ^c (14)	
8.	F-12B1 (CCl ₂ F ₂ Br)	0.952 (12)	31.86 (12)	5.4 (12)		159.7 (12)
9.	F-13B1 (CBrF ₃)		29.417 (14)		6.985 (14)	
10.	F-20 (CH ₃ Cl ₃) Chloroform					
11.	F-21 (CHCl ₂ F)	0.973 (10)	32.080 ^c (9)(6) ^c	6.058 (9)	8.512 (6)	158 ^c (9)

(Continued)

TABLE I (Cont'd.)

1	12	13		
		Compressibility of M(g) at Critical De- composition Temperature and Pressure Z	Uncorrected Heat of Reaction M(g) + H = M(l) + H ($\frac{\text{kcal}}{\text{g-mole}}$)	M(l) + nW(l) = H ($\frac{\text{Btu}}{\text{lb.H}_2\text{O}}$)
23. Nitrogen (N ₂)	0.9991 ^ℓ (24)	M(g) + nW(l) = H ($\frac{\text{kcal}}{\text{g-mole}}$) 12.33 ^ℓ (24)	M(l) + nW(ice) = H ($\frac{\text{kcal}}{\text{g-mole}}$) 3.81 ^ℓ (24)	
24. Oxygen (O ₂)	0.922 ^ℓ (24)	11.84 ^ℓ (24)	3.19 ^ℓ (24)	

(Continued)

ℓ - superscript means that it is evaluated at lower invariant points (with ice)

c - subscript means corrected value

TABLE I (Cont'd.)

1	14					15
	Depression of Critical Decomp. Temp. (°C) by the following Wt. % of NaCl in Solution					
	2	4	6	8	10	
Agent						Sources of Additional Information
1. Ethylene (C ₂ H ₄)						P-T phase equilibrium data (58). Decomp. pressure at 0°C and decomp. temperature at 1 atm. (69).
2. Propylene (C ₃ H ₆)						P-T phase equilibrium data (58).
3. Cyclopropane (c-C ₃ H ₆)						Metastable invariant points and Henry's law constant for cyclopropane in water in a temperature range 0-23°C (42).
4. Propane (C ₃ H ₈)	1.2 (48)	2.4 (48)	3.7 (48)	5.0 (48)	6.3 (48)	Critical decomp. temperature (69). P-T phase equilibrium data (58)(39)(77)(28)(26)(27).
5. Iso-Butane (i-C ₄ H ₁₀)	1.12 (63)	2.30 (63)	3.55 (63)	4.87 (63)	6.23 (63)	Complete phase diagram iso-butane-water system (73).
6. F-11 (CCl ₃ F)						P-T phase equilibrium data for -6.6°C < t < 8.3°C and critical decomp. temperature (14).
7. F-12 (CCl ₂ F ₂)						Complete phase diagram (14).
8. F-12B1 (CClF ₂ Br)	1.04 (12)	2.15 (12)	3.32 (12)	4.54 (12)	5.92 (12)	
9. F-13B1 (CBrF ₃)						P-T phase equilibrium data for -7.0°C < t < 7.2°C and critical decomp. temperature (14).
10. F-20 (CH ₃ Cl ₃) Chloroform						Decomp. pressure at 0°C and decomp. temperature at 1 atm. (69); solubility in water at 25°C (30).
11. F-21 (CHCl ₂ F)	1.12 (10)	2.26 (10)	3.43 (10)	4.63 (10)	5.85 (10)	Heat of solutions (7); solubility as a function of temperature, pressure, and salt concentration (17).
12. F-22 (CHClF ₂)						Complete phase diagram (14).

(Continued)

TABLE I (Cont'd.)

1	14						15	
	Depression of Critical Decomp. Temp. (°C) by the following Wt. % of NaCl in Solution						Sources of Additional Information	
	2	4	6	8	10			
Agent								
13. F-30 (CH ₂ Cl ₂) Methylene Chloride								Decomp. pressure at 0°C and decomp. temperature at 1 atm. (69); solubility in water at 25°C (30); lattice constant (68).
14. F-31 (CH ₂ ClF)	0.97 (9)	2.01 (9)	3.09 (9)	4.24 (9)	5.53 (9)			Solubility as a function of temperature, pressure and salt concentration (17).
15. F-32 (CH ₂ F ₂) Methylene Fluoride								
16. F-40 (CH ₃ Cl)	1.1 (7)	2.3 (7)	3.3 (7)	4.6 (7)	5.9 (7)			Critical decomp. pressure and temperature and P-T phase equilibrium data (20), lattice constant (68).
17. F-40B1 (CH ₃ Br) Methyl Bromide	1.15 (9)	2.39 (9)	3.68 (9)	5.05 (9)	6.57 (9)			Solubility as a function of temperature, pressure and salt concentration (17).
18. F-142b (CH ₃ CClF ₂)	1.10 (12)	2.27 (12)	3.49 (12)	4.77 (12)	6.22 (12)			Solubility as a function of temperature, pressure and salt concentration (17).
19. F-152a (CH ₃ CHF ₂)	0.9 (7)	1.9 (7)	2.9 (7)	4.0 (7)	5.2 (7)			
20. Carbon Dioxide (CO ₂)	0.99 (19)	2.03 (19)	3.13 (19)	4.32 (19)	5.6 (19)			P-T phase equilibrium data for: t < -20°C (71); t > 0°C (56); 4.6 < t < 9.2°C (74), -121.5 < t < -80.7°C (54); complete phase diagram for CO ₂ -H ₂ O system (51).
21. Chlorine (Cl ₂)	0.8 (38)	1.7 (38)	2.9 (38)	4.2 (38)	5.4 (38)			Hydrate composition (78)(3)(22)(21).
22. Hydrogen Sulfide (H ₂ S)								P-T phase equilibrium data (79).

(Continued)

TABLE I (Cont'd.)

1	14	15
Agent	Depression of Critical Decomp. Temp. (°C) by the following Wt. % of NaCl in Solution	Sources of Additional Information
23. Nitrogen (N ₂)		P-T phase equilibrium data for $4.4 \leq t \leq 32.9^\circ\text{C}$ (52); P-T phase equilibrium data of the three phase ice-liquid- hydrate (24).
24. Oxygen (O ₂)		P-T phase equilibrium data of the three phase ice-liquid- hydrate (24).

TABLE II

1	2	3	4	5	6	7	8
Agent	Agent Normal Boiling Point (°C)	Agent Liquid Density at Normal B.P. or at Temp. stated (g/cm ³)	Solubility in H ₂ O at Cr. Decomp. Temp. (wt.%) or at stated condition and dimension	Heat of Solution at Cr. Decomp. Temp. or at stated condition (cal/g-mole)	Hydrate Composition moles H ₂ O moles agent	Hydrate Crystal Structure/Lattice Constant (if any)	Calculated Crystal Density (g/cm ³)
1. Methane (CH ₄)	-161.5 (18)	0.415 ⁻¹⁶⁴ (18)	*0.097 ⁰ (41) d.p.	4561 ⁰ (41) d.p.	7.18 (39)(22)(21)	I (69)	0.915
2. Acetylene (C ₂ H ₂)	-83.6 (18)	0.618 ⁻⁸² (18)	1.1 ⁰ (41) d.p.	4476 ⁰ (41) d.p.	5.7 (22)(69)	I (69)	0.989
3. Ethane (C ₂ H ₆)	-94 (18)	0.546 (53)	0.062 ⁰ (41) d.p.	6439 ⁰ (41) d.p.	8.25 (39)(27)	I (69)	0.958
4. F-12B2 (CF ₂ Br ₂)	24.5 (18)				[17]	[II]	1.33
5. F-22B1 (CHBrF ₂)	-14.5 (18)	1.90 (8)			[17]	[II]	1.12
6. F-41 (CH ₃ F) Methyl Fluoride	-78.4 (18)	0.843 ⁻⁶⁰ (18)			[6] (69)	[I] (69)	1.05
7. Methyl Iodide (CH ₃ I)	42.5 (18)	2.28 ²⁰ (18)	1.38 (41)	8131 (41)	[17] (21)	[II] (69)	1.15
8. F-150a (CH ₃ CHCl ₂)	57 (18)	1.16 (8)	4.3x10 ⁻⁵ (41)	9704 (41)	[17] (69)	[II] (69)	1.04
9. F-160 (C ₂ H ₅ Cl) Ethyl Chloride	13.1 (18)	0.905 (8)	0.447 ⁰ (70)		[17] (69)	[II]/17.2 (69)(68)	0.953

(Continued)

TABLE II (Cont'd.)

1	2	3	4	5	6	7	8
Agent	Agent Normal Boiling Point (°C)	Agent Liquid Density at Normal B.P. or at Temp. stated (g/cm ³)	Solubility in H ₂ O at Cr. Decomp. Temp. and Press. (wt.%) or at stated condition and dimension	Heat of Solution at Cr. Decomp. Temp. and Press. or at stated condition (cal/g-mole)	Hydrate Composition moles H ₂ O moles agent	Hydrate Crystal Structure/Lattice Constant (if any)	Calculated Crystal Density (g/cm ³)
10. F-160B1 (C ₂ H ₅ Br) Ethyl Bromide	38.4 (18)	1.46 ²⁰ (18)	1.056° (70)		[17] (69)	[II] (69)	1.07
11. F-161 (C ₂ H ₅ F) Ethyl Fluoride	- 37.7 (18)	1.226 (8)			8.27 (22)(69)	I (69)	1.15
12. F-1140 (CH ₂ =CHCl) Vinyl Chloride	- 13.9 (18)				[8]	[I trans.]	1.14
13. Argon (A)	-185.7 (18)		1.096° (41) d.p.	3749° (41) d.p.	4.5 (22)(69)	I (69)	1.17
14. Arsine (AsH ₃)	- 55 (18)				6.14 (65)	I	1.36
15. Bromine (Br ₂)	59 (18)	2.928 (18)	5.36 (41)	8487 (41)	8.57 (55)	I/12.01 (69)	1.98
16. Bromine Chloride (BrCl)	5 (69)				[6] (69)	[I] (69)	1.68
17. Chlorine Dioxide (ClO ₂)	10 (18)		2.76x10 ⁻² wt. fr. at 0°C and 1 atm. (70)		6 (69)	I (69)	1.29
18. Hydrogen Selenide (H ₂ Se)	- 41.5 (18)	2.00 (18)	1.2x10 ⁻⁴ wt. fr. at 22.5°C and 1 atm (70)		5.87 (22)(69)	I/12.06 (69)	1.39

TABLE II (Cont'd.)

1	2	3	4	5	6	7	8
Agent	Agent Normal Boiling Point (°C)	Agent Liquid Density at Normal B.P. or at Temp. stated (g/cm ³)	Solubility in H ₂ O at Cr. Decomp. Temp. and Press. (wt.%) or at stated condition and dimension	Heat of Solution at Cr. Decomp. Temp. and Press. or at stated condition (cal/g-mole)	Hydrate Composition moles H ₂ O moles agent	Hydrate Crystal Structure/Lattice Constant (if any)	Calculated Crystal Density (g/cm ³)
19. Krypton (Kr)	-152.3 (18)	2.155 (18)	0.724 ⁰ ₍₄₁₎ d.p.	5015 ⁰ ₍₄₁₎ d.p.	6 (69)	I (69)	1.41
20. Methyl Hydro-sulfide (CH ₃ HS)	6 (18)				[6] (69)	[I]/12.12 (69)	1.15
21. Nitrous Oxide (N ₂ O)	-88.5 (18)		2.3 ⁰ _{d.p.} (41)	6036 ⁰ ₍₄₁₎ d.p.	6 (22)(69)	I/12.03 (69)	1.13
22. Phosphine (PH ₃)	-87 (18)				5.9 (22)(69)	I (69)	1.05
23. Sulfur Dioxide (SO ₂)	-10 (18)	1.434 (18)	**0.15 ¹⁰ _{3.1} (70)		8 (22)(69)	I/11.94 (69)	1.29
24. Sulfur Hexa-fluoride (SF ₆)	-63.8 (18)	1.88 ⁻⁵¹ ₍₁₈₎			17.02 (65)	II (65)	1.16
25. Sulfuryl-Chloride (SO ₂ Cl ₂)	69.1 (18)	1.667 ³⁰ ₍₁₈₎			[17]	[II]	1.13
26. Stibine (SbH ₃)	-17.1 (18)	2.26 ⁻²⁵ ₍₁₈₎			[8]	[I trans.]	1.49
27. Xenon (Xe)	-107 (18)	3.52 (18)	0.192 ⁰ ₍₄₁₎ d.p.	5985 ⁰ ₍₄₁₎ d.p.	6 (69)	I/11.97 (69)	1.77

*Superscript 0 means at 0°C and subscript d.p. means at decomposition pressure of 0°C.

**Superscript means temperature in °C and subscript means pressure in atm.

(Continued)

TABLE II (Cont'd.)

1		9		10		11		12					
Agent		Hydrate Decomp. Pressure at 0°C (mm Hg)	Hydrate Decomp. Temperature at 1 atm (°C)	Hydrate Critical Decomposition		P-T phase relation or P-T phase Equilibrium data for reaction							
				Temp. (°C)	Press. (mm Hg)	M(g) + nW(l) = H		M(g) + H = M(l) + H		M(g) + nW(ice) = H			
						A	B	A	B	A	B		
1.	Methane (CH ₄)	19760 (69)	- 29 (69)				5996 (39)					1029 (39)	
2.	Acetylene (C ₂ H ₂)	4332 (69)	- 15.4 (69)	16 (69)									
3.	Ethane (C ₂ H ₆)	3952 (69)	- 15.8 (69)	14.5 (69)			7164 (39)(60)					2443 (39)(60)	
4.	F-12B2 (CF ₂ Br ₂)			4.9 (9)	386 (9)								
5.	F-22B1 (CHBrF ₂)			9.87 (9)	2012 (9)								
6.	F-41 (CH ₃ F) Methyl Fluoride	1596 (69)		18 (69)									
7.	Methyl Iodide (CH ₃ I)	74 (69)		4.3 (69)	175 (69)								
8.	F-150a (CH ₃ CHCl ₂)	55 (69)		1.5 (69)	70 (69)								
9.	F-160 (C ₂ H ₅ Cl) Ethyl Chloride	201 (69)		4.8 (69)	590 (69)								
10.	F-160B1 (C ₂ H ₅ Br) Ethyl Bromide	115 (69)		1.4 (69)	166 (69)								

(Continued)

TABLE II (Cont'd.)

1	Agent	9 Hydrate Decomp. Pressure at 0°C (mm Hg)	10 Hydrate Decomp. Temperature at 1 atm (°C)	11		12 P-T phase relation or P-T phase Equilibrium data for reaction					
				Hydrate Critical Decomposition Temp. (°C)	Press. (mm Hg)	M(g) + nW(l)		M(g) + H =		M(g) +	
						= H		M(l) + H		nW(ice) = H	
						A	B	A	B	A	B
11.	F-161 (C ₂ H ₅ F) Ethyl Fluoride	530 (69)	3.7 (69)	22.8 (69)							
12.	F-1140 (CH ₂ =CHCl) Vinyl Chloride			1.15 (9)	1366 (9)						
13.	Argon (A)	79800 (69)	- 42.8 (69)					See Ref. (52)		See Ref. (71)	
14.	Arsine (AsH ₃)	613 (69)	- 1.8 (69)								
15.	Bromine (Br ₂)	43.9 (55)		6.2 (62)	93 (62)						
16.	Bromine Chloride (BrCl)	125 (69)	14 (69)								
17.	Chlorine Dioxide (ClO ₂)	160 (69)	15 (62)	18.2 (69)							
18.	Hydrogen Selenide (H ₂ Se)	346 (69)	8 (69)	30 (69)							
19.	Krypton (Kr)	11020 (69)	- 27.8 (69)							See Ref. (71)	

(Continued)

TABLE II (Cont'd.)

1		9	10	11		12							
Agent	Hydrate Decomp. Pressure at 0°C (mm Hg)	Hydrate Decomp. Temperature at 1 atm (°C)	Hydrate Critical Decomposition Temp. (°C)	Hydrate Critical Decomposition Press. (mm Hg)		P-T phase relation or P-T phase Equilibrium data for reaction							
				Temp. (°C)	Press. (mm Hg)	M(g) + nW(l) = H		M(g) + H = M(l) + H		M(g) + nW(ice) = H			
						A	B	A	B	A	B		
20. Methyl Hydro-Sulfide (CH ₃ HS)	239 (69)	10 (69)	12 (69)										
21. Nitrous Oxide (N ₂ O)	7600 (69)	- 19.3 (69)	12 (69)									See Ref. (71)	
22. Phosphine (PH ₃)	1216 (69)	- 6.4 (69)	28 (69)										
23. Sulfur Dioxide (SO ₂)	297 (62)	7.1 (62)	12.1 (62)(20)	1748 (62)(20)		See Ref. (62)(20)		See Ref. (20)				See Ref. (71)	
24. Sulfur Hexa-fluoride (SF ₆)			14.0 (65)	15124 (65)									
25. Sulfuryl-Chloride (SO ₂ Cl ₂)	66 (69)												
26. Stibine (SbH ₃)		10.9 (65)											
27. Xenon (Xe)	1140 (69)	- 3.4 (69)											

TABLE II (Cont'd.)

1	13		14
	Heat of Reaction (Calorimetric)		
	$M(g) + nW(l)$ ($\frac{\text{kcal}}{\text{g-mole}}$)	$M(g) + nW(\text{ice}) = H$ ($\frac{\text{kcal}}{\text{g-mole}}$)	
Agent	Sources of Additional Information		
1. Methane (CH ₄)	14.5 (69)(60)(39)	*4.887 (39)(60)	P-T phase equilibrium relation (39)(49)(52)(60) (38)(26)
2. Acetylene (C ₂ H ₂)	15 (69)		
3. Ethane (C ₂ H ₆)	*17.796 (26)(60)(39)	*3.456 (26)(60)(39)	P-T phase equilibrium relation (60)(39)(58)(26). Hydrate composition (22)(21).
4. F-12B2 (CF ₂ Br ₂)			
5. F-22B1 (CHBrF ₂)			
6. F-41 (CH ₃ F) Methyl Fluoride	18 (69)		
7. Methyl Iodide (CH ₃ I)	31.4 (69)		
8. F-150a (CH ₃ CHCl ₂)	29.4 (69)		
9. F-160 (C ₂ H ₅ Cl) Ethyl Chloride	31.9 (69)		Hydrate composition (21).
10. F-160B1 (C ₂ H ₅ Br) Ethyl Bromide	38 (69)		

(Continued)

TABLE II (Cont'd.)

1	13			14
	Heat of Reaction (Calorimetric)		Sources of Additional Information	
	$M(g) + nW(l)$ ($\frac{\text{kcal}}{\text{g-mole}}$)	$M(g) + nW(\text{ice}) = H$ ($\frac{\text{kcal}}{\text{g-mole}}$)		
11. F-161 (C ₂ H ₅ F) Ethyl Fluoride	18 (69)			
12. F-1140 (CH ₂ =CHCl) Vinyl Chloride				
13. Argon (A)				
14. Arsine (AsH ₃)			Decomposition pressure at 21°C (65).	
15. Bromine (Br ₂)	20.83 (55)		Hydrate composition (2)(62)(22)(21)(44)(80). Structure of Bromine Hydrate Crystal (45).	
16. Bromine Chloride (BrCl)			Hydrate composition (3).	
17. Chlorine Dioxide (ClO ₂)	16.5 (69)			
18. Hydrogen Selenide (H ₂ Se)				
19. Krypton (Kr)	13.9 (69)			

(Continued)

TABLE II (Cont'd.)

1		13		14
Agent	Heat of Reaction (Calorimetric)		Sources of Additional Information	
	$M(g) + nW(l)$ ($\frac{\text{kcal}}{\text{g-mole}}$)	$M(g) + nW(\text{ice}) = H$ ($\frac{\text{kcal}}{\text{g-mole}}$)		
20. Methyl Hydro- Sulfide (CH ₃ HS)	16.6 (69)			
21. Nitrous Oxide (N ₂ O)	14.7 (69)			
22. Phosphine (PH ₃)			Decomposition pressure at 1°C and 25°C (65).	
23. Sulfur Dioxide (SO ₂)	16.6 (69)		P-T phase equilibrium data (20).	
24. Sulfur Hexafluoride (SF ₆)	**29.57 (65)	**5.14 (65)		
25. Sulfuryl- Chloride (SO ₂ Cl ₂)	31 (69)			
26. Stibine (SbH ₃)				
27. Xenon (Xe)	16.7 (69)			

*Evaluated at lower invariant point, uncorrected value.

**Evaluated at critical decomposition pressure and temperature, uncorrected value.

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THE ANOMALOUS GROWTH OF ICE CRYSTALS IN FLOWING WATER AND NaCl SOLUTIONS

(John Vlahakis)

INTRODUCTION

The growth of ice crystals in water and aqueous solutions is of interest in fields as diverse as cryobiology, cloud physics, and desalination by freezing. It is to the latter field that we have directed our attention.

The main purpose of this work was to obtain basic data on the growth rate of ice in flowing subcooled water and aqueous NaCl solutions under well defined hydrodynamic conditions. An understanding of growth under these experimental conditions will help lead to an understanding of ice growth in freezers used for desalting sea and brackish waters and also may help clear up much disagreement in the literature on the nature of ice growth.

In earlier studies, Fernandez (F-2,F-3,F-4,F-5) developed a theoretical model for ice crystal growth in flowing subcooled water. The resulting equation fitted the data well for water velocities between 1 and 46 cm/sec, with subcoolings ranging from 0.02 to 0.70°C, but predicted zero growth at zero water velocity. The model assumed that the growth rate is determined solely by the rate at which the latent heat of solidification is transferred by convection from the crystal tip to the flowing water, and transport rates were predicted from boundary layer theory.

Our work is thus an extension of the earlier studies in an attempt to locate the onset of the region where other mechanisms become significant factors in the heat transfer process, within the limits of our apparatus. Since the velocity experienced by a particle in a freezer is on the order of 0.01 to 1 cm/sec, and this is also the region which the previous works do not fully investigate, we studied distilled water velocities from 1 cm/sec down to the lowest velocities possible with the apparatus, 0.04 cm/sec.

The earlier studies by Barduhn and Fernandez failed to explain the ice crystal growth rate data in flowing NaCl solutions. The experimentally observed growth rates with increasing NaCl concentration were greater than those predicted by a heat and mass transfer analysis. (The analysis was an extension of the convective heat model of pure water, but with the diffusion of salt from the interface taken into account.) At 2% NaCl concentration, for example, the observed growth rate averaged 35% above the predicted value but still less than that in pure water. Data at 4% and 6% NaCl were in somewhat closer agreement with the theory. No adequate explanation could be advanced for this phenomenon.

In addition, experimental evidence of many other workers indicates enhanced growth rates over those in pure water under special conditions in more dilute aqueous solutions. The proposed mechanisms given in the literature for this anomaly are highly contradictory, quite confused, and altogether unsubstantiated.

In order to investigate this effect more rigorously, growth rates were measured at five NaCl concentrations: 0.15, 0.50, 0.90, 2.0, and 6.0% wt. At each concentration at least three solution velocities were employed to determine the effect of forced convection: 0.20, 0.85, and 3.9 cm/sec.

For all cases, both pure and salt water, subcoolings ranged from 0.05 to 0.9°C. Typical subcoolings in freezers for desalting sea and brackish water are also less than 1°C. This is due mainly to the need to limit nucleation

and thus increase particle sizes, but it also reduces refrigeration costs.

Our experimental system consisted of a fixed single crystal in free growth with subcooled water or salt solutions flowing past it. We thus had three independent variables, solution velocity, V , subcooling, ΔT , and solute concentration, W , affecting the dependent variable of ice crystal linear growth rate, v . Like the previous work done in this laboratory, the growth rates measured were along the a -axis or parallel to the basal plane. This is the faster growth direction. c -axis growth, or growth perpendicular to the basal plane was not investigated in this work.

LITERATURE SURVEY

This literature review is divided into two major sections. The first deals with ice crystal growth in distilled water, the second is concerned with growth in aqueous solution. The first section is divided further into a separate discussion of forced convection experiments in distilled water, a brief word about unconfined growth rate experiments in quiescent water, and a review of Fernandez' model of ice growth in a forced convection system.

The second section begins with a review of ice growth rate measurements in capillary tubes in the presence of solutes. We then point out the major work done in unconfined growth, first in quiescent solution and then in forced convection systems.

For a timely, comprehensive review of the structure and properties of ice see Fletcher (F-7). Although we are not directly involved with this aspect of ice growth, it will, of course, help to form a more thorough understanding of this phenomenon.

1. Forced Convection Experiments in Pure Water

The distilled water ice growth data of Fernandez were taken at water velocities ranging from 1.3 to 46 cm/sec. Assuming for each water velocity a growth law of the form

$$v = a' \Delta T^n \quad (1)$$

a least squares fit yielded the results shown in Table 1.

Table 1 shows that while Fernandez' work established that the exponent on ΔT was $3/2$ for water velocities of 8 cm/sec and above, the exponent tended to increase at the lower water velocities. Fernandez assumed that $n = 3/2$ exactly and recalculated the experimental coefficients, a' , for water velocities 8 cm/sec and above. The coefficients were found to depend on the square root of velocity within experimental error. The fit of the resulting equation

$$v = a V^{1/2} \Delta T^{3/2} \quad (2)$$

where a is a constant, is shown in Figure 1. It is easily seen that the data at the higher water velocities (filled circles) are in excellent agreement with the above equation when $a = 0.0466 \text{ cm}^{1/2} \text{ sec}^{-1/2} \text{ } ^\circ\text{C}^{-3/2}$.

The question arose as to whether the scattered data and changing exponents at the lower velocities represented a change in mode of growth, or whether inadequate experimental technique was responsible. To help answer this question Poisot (P-1) refined the work of Fernandez by redesigning the crystal growth cell system so that the water velocity at the crystal tips was

more accurately known. He extended the previous study by investigating water velocities from 1 to 16 cm/sec. As shown by Table 2, Poisot confirmed that $n = 3/2$ down to the velocity of 1 cm/sec. The trend of rising exponents on ΔT reported by Fernandez in this experimental range was thus only apparent rather than real.

While Bibikov (B-2) and Bukina (B-4) also measured ice growth rates in forced convection, Farrar and Hamilton (F-1) were the first to present reasonably consistent results of growth along the a-axis. They worked at water velocities of 0, 1.78, 10.0, 16.1, and 29.0 cm/sec and at subcoolings between 0.01 and 1.0°C. The data can be fit to an equation of the form

$$v = a' \Delta T^n \quad (1)$$

at each velocity. Table 3 shows the coefficient and exponent found in each case.

It is noted that the exponent is close to $3/2$ for all but zero water velocity, in general agreement with Fernandez and Poisot. Indeed, the raw data of Farrar and Hamilton, when plotted on a graph of $v/v^{1/2}$ versus ΔT , agree well with those of Fernandez within experimental error (Figure 1).

Huige and Thijssen (H-8) have done similar experiments using an apparatus like Fernandez. Their results in flowing water are shown in Table 4. The exponents are seen to be near $3/2$ again, with the exception of the value at the lowest flow velocity of 0.80 cm/sec.

Huige and Thijssen maintain that a tendency toward a maximum growth rate exists at higher water velocities, particularly at low supercoolings. Their results seem quite scattered, however, and they do not investigate velocities above 21.2 cm/sec. The raw data points are not reported and so are not available for a more detailed comparison with the work of others. Furthermore, their method of measuring temperatures is not explained.

However, Fernandez' work at the higher velocities (8 cm/sec to 46 cm/sec) established the square root law most firmly. His work showed that at high velocities where heat transfer rates are high, convective heat transfer still controls the growth rate. Therefore, the growth rate continues to rise as the $1/2$ power of the velocity and heat transfer remains the only resistance involved. If the growth rate ceases to increase as velocities exceed 21 cm/sec, as Huige and Thijssen think, this would indicate that the mechanism of molecular deposition (called a kinetic mechanism) at the ice surface is indeed an important factor.

More accurate data in the water velocity range of 20 to 50 cm/sec would have to be taken by Huige and Thijssen before there would be any possible basis for serious disagreement with the convective heat transfer theory. The theory will be reviewed in a following section.

2. Quiescent Water-Experiments in Free Growth

The increase in exponent on ΔT from $3/2$ to 1.8 in Fernandez' data as the water velocity decreased was thought significant due to two factors. Not only does Fernandez' growth law predict zero growth in quiescent water, but also other workers have found that the exponent on ΔT is near 2 for growth in quiescent water. There is ample evidence in the literature, therefore, for thinking that an increase in exponent as the velocity approaches zero indicates a change in mode of growth. Some data on free growth of dendrites in quiescent water are shown in Table 5.

Alternate of additional mechanisms of latent heat transfer from the interface which may become important as the velocity decreases are heat conduction in the solid and natural convection at the tip of the platelet. It is quite conceivable that with decreasing water velocity, a transition region will be observed.

3. Fernandez' Model of Ice Growth in a Forced Convection System

Fernandez has presented a simplified model of ice growth in flowing solutions and compared it with his experimental results. Heat and mass transfer rates to the stagnation line of a two-dimensional cylindrical platelet with parabolic cross-section were calculated according to boundary-layer theory. The ice in the region surrounding the platelet tip is assumed to be isothermal. The growth rate and the tip radius of curvature are expressed as functions of sub-cooling by utilizing the maximum velocity principle, to be discussed later.

The boundary layer equations have the form:

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} = 0 \quad (\text{Continuity}) \quad (3)$$

$$u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} = U \frac{\partial U}{\partial x} + \nu \frac{\partial^2 u_x}{\partial y^2} \quad (\text{Motion}) \quad (4)$$

$$u_x \frac{\partial T}{\partial x} + u_y \frac{\partial T}{\partial y} = \alpha \frac{\partial^2 T}{\partial y^2} \quad (\text{Energy}) \quad (5)$$

$$u_x \frac{\partial w'}{\partial x} + u_y \frac{\partial w'}{\partial y} = D \frac{\partial^2 w'}{\partial y^2} \quad (\text{Diffusion}) \quad (6)$$

where $U = U(x)$ is the potential velocity distribution around the parabolic cylinder, and $w' =$ mass fraction of salt.

All the heat liberated on freezing was assumed transferred to the liquid side of the interface. Thus:

$$v\rho_i L = -k \left(\frac{\partial T}{\partial y} \right)_{y=0} \quad (7)$$

This is an important assumption. Since Fernandez showed that kinetic resistances to ice deposition are not present under the conditions studied, the interface temperature is thus taken to be the equilibrium temperature for bulk ice (i.e. 0°C) less the depression due to the curvature of the interface. Since the curvature of a parabola varies strongly and has a maximum value (minimum radius) at the tip, the coldest spot in the ice crystal is at the tip and other interfacial points are progressively warmer as one moves away from it. Temperature gradients must, therefore, exist in the ice and produce a heat flux at the tip in addition to that caused by tip growth. Equation 7 assumes that this additional flux may safely be neglected. An equation expressing the ice growth velocity in terms of solution velocity, tip radius, and the temperature difference between the ice-water interface and the bulk liquid was then derived:

$$v = c' \frac{V^{1/2}}{R^{1/2}} (T_i - T_\infty) \quad (8)$$

where $c' = kA/(\rho_i L v^{1/2})$, A being a dimensionless temperature gradient at the ice-water interface, a function of the Prandtl number only.

For pure water, the interface temperature can be expressed as

$$T_i = T_M - \frac{\gamma T_M}{\rho_i L R} - \delta T \quad (9)$$

The second term to the right of the equals sign is the equilibrium freezing point depression due to the interfacial curvature, the third term taking into account a possible driving force for kinetic deposition. In addition, for salt solutions, the interface temperature is reduced by the presence of salt.

Letting $\Delta T = T_M - T_\infty$, and $\beta = \frac{\gamma T_M}{\rho_i L}$, we get

$$v = c' \frac{V^{1/2}}{R^{1/2}} (\Delta T - \delta T - \frac{\beta}{R}) \quad (10)$$

for pure water.

The maximum velocity criterion is then used to determine the unique radius of curvature where $v = v_{\max}$. This is done by differentiating the above equation with respect to the radius of curvature. Substitution of the expression for the unique radius of curvature,

$$R = 3\beta/\Delta T \quad (11)$$

into Equation 10 yields

$$v = a V^{1/2} (\Delta T - \delta T)^{3/2} = \frac{2kA V^{1/2}}{\sqrt{27\gamma T_M \rho_i L v}} (\Delta T - \delta T)^{3/2} \quad (12)$$

Since the kinetic resistance was found to be negligible, even at the highest water velocities studied, Fernandez took

$$\delta T \ll \Delta T.$$

Then

$$v = \frac{2kA}{(27\gamma T_M \rho_i L v)^{1/2}} V^{1/2} \Delta T^{3/2} \quad (13)$$

For the case of salt, Fernandez derived

$$v = \frac{a}{1+b} V^{1/2} \Delta T^{3/2} \quad (14)$$

where $a = 2kA/(27\gamma T_o L_v)^{1/2}$ in both Equations 12 and 14, and b is a constant whose value depends nearly linearly on the concentration of salt in solution. At this time, several observations can be made relating to the above derivation. Each topic will be more completely discussed in later sections. We point out that for a given degree of subcooling and specific solution velocity, the addition of salt is predicted always to decrease the ice growth rate below its pure water value. In no case is it predicted that the addition of salt increases the growth rate.

By means of Equation 13, and our knowledge of the experimental value of the coefficient a , we can calculate a value for γ , the ice-water interfacial tension. Using the value $a = 0.0466 \text{ cm}^{1/2}\text{sec}^{-1/2}\text{C}^{-3/2}$, $\gamma = 31.8 \text{ ergs/cm}^2$ in good agreement with some of the values reported in the literature.

Zener (Z-1) first used the "maximum linear velocity of phase transformation" to predict that the product of the square of the spacing between lamellae of cementite and ferrite and the growth velocity should be constant. His work has been verified by others, including Jackson and Hunt (J-1). The maximum velocity criterion has no truly theoretical justification, but it is used because it gives results which are usually consistent with experimental observations.

4. Discussion of Ice Crystal Growth in Aqueous Solution

a. Capillary Growth

While Turmlirz (T-6) was the first to measure the growth rate of ice in supercooled water in 1894, it was not until 1916 that experiments were performed to determine the effect of various solutes upon the growth rate in water. Walton and Brann (W-1,W-2) studied ice growth in solutions of more than 50 different compounds including inorganic chlorides and nitrates, alcohols, sugars, dyes, and colloids. The experimental method was to introduce an L-shaped 7 mm I.D. tube filled with solution into a constant temperature bath held at -9.1°C for concentrations of solutes ranging from 0.02M to 0.5M. After 3-4 minutes a seed was introduced and the crystal was timed for a distance of one meter.

The authors reported that all the solutes retarded the velocity of crystallization. "In no case has acceleration been observed". Interestingly, however, a small enhancement is noted from a table of Walton and Brann's raw data for 0.02M HCl. The growth rate in the HCl solution was reported as 15.8 sec/m (6.33 cm/sec) compared to 16.3 sec/m (6.14 cm/sec) for pure water. Although their experimental error can be estimated to be on the order of 1 sec/m (equivalent to 0.4 cm/sec), the reported values for HCl can hardly be described as a retardation.

The first reported enhancement of ice crystal growth rate was made by Brann in 1918, having extended the work of Walton and Brann. Working with many different substances and various concentrations at a temperature of -7°C , Brann found that concentrations of 1 and 2% ferric hydroxide increased the growth rate by 55% over the pure water value. This was the only substance studied which increased the growth rate. Brann explains the anomaly totally on the basis of a change in the crystal habit. Only with ferric hydroxide did the ice crystals exhibit a needle-like form which had a "straightforward shooting movement down the length of the tube". In all the other experiments the crystal grew in a spiral movement around the inside of the tube. Brann's contention in this paper was that the retardation of crystal growth rates, in general, was due to

the hydration of the solute. The one example of increased growth rates, of course, was totally unexpected and thus conveniently left ungraphed in their figure of results.

The above papers represent work of little significance since their results depended on the bore of the capillary tube and the additive concentration was usually so high that the measured growth rate reductions may have indicated solely freezing point lowering effects due to solute rejection at the interface.

In 1935 Tammann and Buchner (T-1) presented the first experimental evidence of maxima in the ice growth rate as a function of solute concentration, with subcooling as a parameter. Their data are re-plotted in Figure 2. Again, capillary tubes (1.2 mm I.D.) were immersed in a constant temperature bath, and the crystal was timed for a distance of 80 mm. These workers were able to investigate the effects of subcooling and solution concentration on the growth rate in a more systematic manner than the previous group. In the very dilute solutions the buildup of rejected solute most likely was not important and the anomaly could be easily seen. For NaCl the maximum growth rate occurred at about 0.1-0.2% and became more pronounced with increased subcooling. The anomaly was explained by saying that the addition of solute caused an acceleration of the transformation of molecules into "ice forming ones". At the interface, then, the solute has caused a comparatively high concentration of the ice forming molecule type and the growth rate is increased. Since the addition of solutes actually disturbs the relatively high structural order of subcooled water, in general, this explanation seems grossly inadequate, especially since the presence of solute actually decreases the water concentration at the growing interface.

There are two other works which deal with the effects of aqueous solutions on ice growth in capillaries. Michaels, Brian, and Sperry (M-4) in 1966 and Pruppacher (P-7) in 1967 both confirmed Tammann and Buchner's observations that an enhancement of growth rate is confined to a certain concentration interval, is more pronounced at larger subcoolings, and is dependent on the type of solute. Michaels, Brian, and Sperry used dilute solutions of salts, surfactants, and water-soluble polymers at interfacial subcoolings of 0.03°C to 0.2°C. Of the salts investigated they reported that NaCl, CsF, and NH_4F at 10^{-4} M had no effect on the growth rate at relatively low subcoolings, but revealed some enhancement at the highest subcoolings studied. At 10^{-4} M concentration CsI produced about 100% enhancement over the entire range of experimental subcoolings, while NH_4I at the same concentration reduced the growth rate by a factor of 4 at low ΔT to a factor of 2 at high ΔT . At 10^{-5} M concentration, however, NH_4I behaved much like the other salts did at 10^{-4} M. Interestingly, the authors postulated that the NH_4I effect of reducing growth rate at 10^{-4} M concentration might be due to the preferred orientation of water molecules by the interface freezing potential of Workman and Reynolds (W-4). [For a comprehensive review of freezing potential, see Gross (G-1)]. This was thought to be a special case since growth rate enhancement was such a strong function of subcooling and not type of solute. For example, both 0.1% polyvinyl methyl ether and 0.01 wt.% polyvinyl alcohol had no effect at low ΔT , but doubled the growth rate at high ΔT , just like salts. As a general mechanism the additives were thought to be responsible for introducing dislocations at the interface

thus increasing the growth rate. It is perhaps possible, but highly unlikely, that dilute solutions could affect the already fast kinetics enough to increase observed growth rates by a factor of 3 or 4 in some cases. Fernandez showed that for pure water velocities even as high as 46 cm/sec the growth rate was determined by heat transfer, not kinetics. Fernandez' results clearly show that growth rate enhancement on kinetic grounds has no support since kinetic resistance is completely absent. The interface freezing potential effect observed by Workman and Reynolds is due to the selective incorporation of ions in the ice. Michaels, Brian, and Sperry assign the reduction of growth rate by 10^{-4} M NH_4I to this mechanism, but another paper, to be discussed later, will attribute the opposite effect to the freezing potential.

Pruppacher, using polyethylene tubes of 1.2 mm I.D., grew ice in salt solutions of concentration between 10^{-6} and 10^{-1} M in the subcooling range of 1° to 15°C . At concentrations larger than 0.05 M all the salts studied reduced the growth rate of ice below its pure water value. At concentrations below 0.05 M most of the salts had no effect. The fluorides (KF , CsF , NaF), however, increased the growth rate with the maximum occurring at 0.01 M and the effect became more pronounced at larger subcoolings. Pruppacher suggests that since the width and thickness of the dendrites were observed to be less in solution than in pure water an increased rate of heat dissipation results from the smaller radius of curvature at the tip. He neglects to say why this should only be true in fluoride solutions, however. Also, since salts raise the interfacial surface tension, his explanation that they are adsorbed everywhere but at the tip of the crystal is not sound. There should be a deficiency rather than adsorption at the interface.

b. Capillary Versus Free Growth

The investigation of growth rates in capillary tubes is of dubious value since the results are difficult to interpret and are not useful for translating into free growth in a stirred tank reactor. The reasons for this follow.

In constrained growth, the effect of the wall is uncertain, but it acts to direct the growing crystal and obviously affects the growth rate whenever it is in direct contact with the ice. Also, one cannot directly measure the liquid temperature in contact with the crystal in the capillary. Only the bath temperature can be measured. The true subcooling is obscured and the exact analytical solution for the interface temperature is essentially unsolvable. Moreover, in confined growth the solute field is just as vague as the thermal field. In capillary growth we also cannot vary solution velocity, of course.

Unconfined growth in a large tube has the advantages of simple, reasonably well known hydrodynamics, a directly measured melt temperature, and the use of solution velocity as an independent variable.

In the next section we will discuss free growth, first in quiescent solution and then in forced convection systems.

c. Free Growth-Quiescent Solution

Lindenmeyer (L-1) [also Lindenmeyer and Chalmers (L-2)] studied the free growth rate of ice along the basal plane in 10^{-3} , 10^{-1} , and 1 M quiescent aqueous solutions of KCl , acetic acid, and sugar at subcoolings

ranging from 1 to 7°C. The solutes at concentrations of 0.01 M produced an increase in growth rate, none of the solutes affecting the growth rate at the lower concentration. They decreased the growth rate at 1 M. These observations are basically in line with Pruppacher's work in capillaries mentioned above. Lindenmeyer proposed that the ice growth rate behavior could be correlated with the diffusion of solutes away from the advancing interface. However, the addition of mass transfer resistance cannot account for an increase in growth rates above the pure water value. Although the solute with the highest diffusion coefficient yielded the highest growth rate among these few solutes, this does not explain any enhancement.

Pruppacher's (P-5) results on the free (unconfined) growth rate of ice in quiescent dilute solutions of salts between 10^{-5} and 10^{-1} M concentrations showed agreement with his observations of growth in polyethylene capillary tubes. NaF, CsF, and KF again enhanced the growth rate, the maximum occurring around 10^{-2} M. The other salts studied had no effect on the growth rate in this concentration range. All of the salts invariably depressed the growth rate at concentrations above 10^{-2} M. The author discusses possible mechanisms of enhancement including adsorption of solute atoms and electric field effects. He notes, however, that Workman and Reynolds (W-5) observed the strongest electrical effects at bulk concentrations of between 10^{-5} and 5×10^{-4} M where no growth rate enhancement was noted.

In 1968 Ryan and Macklin (R-2) measured the component free growth rates of ice in quiescent 10^{-1} M solutions of KF, CsF, LiI, and sucrose and 10^{-3} , 10^{-2} M solutions of LiI supercooled from 1 to 6°C. The growth rate normal to the basal plane was enhanced in all the 0.1 M solutions. The growth rate parallel to the basal plane was enhanced with the two fluoride solutions but depressed by the LiI and sucrose solutions. The growth rate enhancements by the fluorides is not unexpected in view of Pruppacher's work, but Ryan and Macklin achieve the effect at a concentration which is an order of magnitude higher than Pruppacher. At 10^{-1} M KF and CsF, Pruppacher observed depression of growth rates. The authors conclude that understanding the effect of solute adsorption as well as the effect of the interface potential is needed to explain the anomalous behavior. They attributed the rate increase in fluoride solutions to an excess of cations at the interface enhancing the mobility of water molecules.

Ryan (R-3) extended this work in 1969 to 10^{-2} M solutions of LiF, NaF, KF, and AlF_3 at low subcoolings (0.1°C to 2.5°C) to check the results of Ryan and Macklin and Pruppacher. All of these solutes enhanced the growth rate. But Ryan states that the enhancement effect does not occur in solutions of metal chlorides, bromides, or iodides. He then suggests that only those salts (metal fluorides) which produce a comparatively large potential at the interface are able to increase the growth rate. As a mechanism, "...a preferential orientation of the water molecules by the interface freezing potential" was proposed.

In the light of the papers already reviewed, both the judgement of attributing enhancement solely to metal fluorides and the proposed mechanism of this effect are unrealistically restrictive and fail to explain any work except perhaps Pruppacher, some of Macklin and Ryan, and Ryan. This explanation could not even explain the data of Tammann and Buchner taken

35 years previously. Furthermore, Huige and Thijssen (H-8) observed increased free growth rates of ice in quiescent glucose solutions at low concentrations. The experiments were carried out at subcoolings from 1 to 5°C and showed about a 27% increase in rate at $\Delta T = 1^\circ\text{C}$, and 1.12% glucose. Glucose, like many of the solutes previously discussed, is neither a metal fluoride nor is it ionizable, obviously.

d. Free Growth in Solution-Forced Convection

Several papers have indicated the anomalous effects of dilute NaCl solutions in a forced convection system. Johnson et al (J-2) worked with a direct freeze separation process to desalinate sea water. Tests were made on the effect of ΔT and brine concentration on ice crystal size produced in a continuous stirred reactor. Average particle diameter and average brine salinity were measured for a certain growth period, agitator speed, and ΔT . The results are plotted in Figure 3 and show the rapid increase in growth rate at 0.55% NaCl.

Farrar and Hamilton, growing single crystals, observed an average of about 50% higher growth rates in 0.3% NaCl solutions flowing at 1.78 cm/sec than in pure water at the same velocity. The subcoolings ranged from 0.01 to 1°C. Their data as well as those of Fernandez in salt solutions are shown in Figure 4 and are compared to the theory of simultaneous heat and mass transfer given by Fernandez. (Fernandez worked at solution velocities of 12 cm/sec at 2 and 4% NaCl, and 8 cm/sec at 6% NaCl.) All the data in this figure have been plotted as a' versus concentration where a' is the coefficient in Equation 2. The plot assumes the growth rate dependence on velocity and subcooling to be the same as in distilled water, $1/2$ and $3/2$ power, respectively. The data in this form do not fit the theoretical curve especially at the lower salt concentrations. Fernandez' data at 2% NaCl is an average of about 35% higher than his predicted value.

The papers on ice growth in flowing NaCl solutions, as well as those on free and capillary growth in various dilute quiescent solutions point to anomalous growth rates with several things in common. The growth rate versus concentration has a maximum, the anomaly is located within a dilute concentration range, the effect is not very solute specific, and the maximum is more pronounced with increased subcooling. Another observation is also clear. No simple, concise qualitative explanation has yet been advanced to explain the phenomenon completely with respect to all of the data available, and no quantitative explanation has even been proposed.

APPARATUS AND PROCEDURES

The constant temperature coolant bath, water or solution reservoir, and measuring and recording apparatus have been described previously by Poisot and Fernandez. The crystal growth cell is basically the same as Poisot's with one exception. The glass flow tube is not in contact with the main aluminum body in our cell. Instead, there is a $1/2$ " thick styrofoam layer between glass tube and aluminum block. This was one of the first modifications performed on Poisot's equipment as a result of our investigations on the effect of cell coolant temperature on crystal growth rate. It was found that for water velocities below 1 cm/sec, axial and radial temperature gradients in the cell

began to influence the measured crystal growth rates. As the next step in reducing these gradients, a simple system was devised in which coolant was pumped into a small holding tank so that it would warm to some extent. From there it was pumped into the cell. Since these measures were found to be inadequate, it was decided to accurately control the temperature of the coolant.

The achievement of nearly adiabatic conditions requires the matching of the coolant temperature with the temperature of the incoming subcooled solution. This was accomplished by modifying the apparatus as shown in Figure 5A.

The modification consists in having the coolant fluid pass through a heat exchanger coil immersed in a constant-temperature bath prior to entering the ice crystal growth cell. The temperature of the bath, and hence also that of the cooling fluid, is controlled by a mercury thermoregulator and an electronic relay in conjunction with a heater element. Two precision mercury thermometers, graduated in $1/20^{\circ}\text{C}$, are used to monitor the temperatures of both the coolant and the test solution entering the cell.

By means of this modification, maximum axial temperature gradients in the cell were reduced to less than $0.05^{\circ}\text{C}/\text{ft.}$ at a solution velocity of $0.5 \text{ cm}/\text{sec}$ and to about $0.10^{\circ}\text{C}/\text{ft.}$ at $0.1 \text{ cm}/\text{sec}$.

Other modifications consisted of the installation of a solution by-pass for low velocity work, and the attachment of a heat exchanger at a point in the solution line just before the cell entrance. These improvements allow a greater flexibility in being able to select different degrees of subcooling at a specific solution velocity. They also let us run at higher solution reservoir temperatures so that the problem of nucleation in the tank is largely circumvented.

A constant voltage transformer was installed in the line to the solution reservoir stirrer. This also prevented possible nucleation in the tank by eliminating speed variations of the agitator.

We will now discuss the standard run procedure, special run techniques, and the experimental determination of the equilibrium temperature of a crystal.

It is noted that all standard calibration procedures were done in the same manner as Fernandez and Poisot.

1. Standard Run Procedure

The solution reservoir is filled and 5-6 hours are allowed for the steady-state temperature to be reached. Subsequently, the coolant heat exchanger bath is turned on by setting the thermoregulator to the appropriate reading, switching on the electronic relay control, the variable speed stirrer, and the coolant pump. While the temperature of the coolant flowing through the cell is coming to steady-state, the reference ice bath is prepared and the reference junction is immersed in it via a glass sleeve. The ice seeding unit (see Figure 5B) is also prepared and slipped onto the bushing, which is either aluminum or plastic, depending on the experimental temperature to be employed. The points between the copper wire and glass capillary and between the glass capillary and rubber stopper are sealed with paraffin. The path of the traveling microscope is adjusted to be parallel to the axis of the capillary tube. A container of room-temperature distilled water is set in place for later use in melting back the ice for continuous operations. Liquid nitrogen is then poured into the small Dewar flask in which the copper wire from the capillary is immersed. The solution from the subcooled reservoir is

siphoned into the lines and by manipulation of the rotameter by-pass, all visible air bubbles are removed from the system.

The solution flow rate is adjusted by means of the needle valve. The temperatures of the incoming coolant and incoming solution are monitored and adjustments made in the coolant heat exchanger outlet temperature. The solution temperature also may be adjusted by changing the cell by-pass flow rate and the coolant flow rate to the precooler, if required. The temperature of the solution stream, observed on the thermocouple recorder, should then check with the thermometer readings within about 0.05°C . The thermocouple can then be pushed forward or pulled backward 3" - 6", depending on its initial position, in order to check on the magnitude of the axial gradients. The thermocouple sheath can also be turned 360° to note radial gradients.

The level of the liquid nitrogen in the Dewar flask and the degree to which this flask is covered are adjusted so that the ice seed is created only when the temperature in the flow tube has reached a steady state value. Growth rate data are taken after the ice has passed the tip of the capillary. It is optional whether the liquid nitrogen is taken away from the copper wire during the run, since we have shown this not to affect the measured growth rate.

When the data have been completed, the solution flow is stopped and warm water is siphoned through the flow tube to melt back the crystal. After this has been accomplished, the solution flow is once again turned on, and the procedure is repeated.

Much practice is needed both to develop a solution flow with minor temperature gradients and also to create an ice seed at precisely the correct time during the run. Good timing is required because the ice crystal must grow into the flowing solution only after a steady state temperature of experimental interest has been attained. Otherwise, troublesome temperature gradients result in meaningless data.

For work at low solution velocities and high salt concentrations, two methods have been used to help delay the appearance of the seed. For one, the copper wire in the capillary tube is retracted 1 or 2 cms to increase the temperature at the tip of the wire. Also, when working with 6% NaCl solution at velocities of 0.20 and 0.85 cm/sec, a solution of approximately 2.5% NaCl is put into the capillary tube. Aluminum chips were glued to the copper wire tip to help nucleate a seed. The aluminum chips are needed because it is much more difficult to nucleate a crystal in salt water than in pure water. The 2.5% NaCl solution has a dual purpose. First, of course, the solution helps delay the seed just because it is not as thermodynamically subcooled as pure water at run conditions.

Secondly, it helps the crystal grow out of the capillary in a more morphologically well defined manner. When using pure water in the capillary, the seed would "explode" beyond the capillary tip. Nucleation throughout the flow tube would set in and plugging would result before growth rate measurements could be taken.

2. Special Techniques

Getting data at relatively low solution velocities combined with values of high salt concentrations proved difficult when employing the standard operating procedure. The difficulties arise from the low temperatures which must be attained leading to problems in timing the arrival of the seed and problems with extraneous crystal growth in the cell. Therefore, several special run

techniques were introduced to accelerate the production of data.

At solution velocities of 0.20 and 0.85 cm/sec and a concentration of 2% NaCl, the overshoot method was used. This simply involved increasing the solution velocity to between 10% and 20% above the desired steady state value. As the appropriate degree of subcooling was being approached, the flow rate would slowly be decreased until it had reached the experimentally desired value. This not only allowed us to time the arrival of the seed more easily, but also increased data production.

At the same two velocities but at 6% NaCl the overshoot method was modified slightly. In one variation, we overshoot the flow rate by about 100%. As the ice crystal begins to advance in the capillary tube, the flow rate reading is abruptly decreased to the appropriate value. This causes the steadily rising subcooling to remain constant for a period of time while the crystal is growing into the melt. This is called the overshoot-shock technique.

The overshoot-shock technique is advanced one step further. This is the "continuous overshoot-shock" procedure and requires maintaining the solution reservoir at a temperature somewhat above that which would be needed normally for a 6% salt solution flowing at 0.20 cm/sec. We employ basically the overshoot-shock method as above, but then increase the flow rate to a value above the desired steady-state value (to about 0.4 cm/sec. for instance) after the growth rate data has been taken. Due to heat buildup in the lines, this increase in flow rate causes the temperature in the cell to rise temporarily. The crystal then begins to recede, but the increased flow rate eventually leads to cooler temperatures.

This then increases the subcooling once more and the crystal grows out of the capillary tip again. We then "shock" or fix the subcooling at the appropriate value by setting the flowmeter to the correct value, and the process is repeated. On the temperature recorder this method traces out something like a truncated sine wave. It should be stated that the temperature at the "top" of these sine waves can remain constant for about two minutes. An advantage of this method is that a relatively rapid series of measurements or "passes" can be produced at similar temperatures, and crystal seed timing is not as critical a factor. An additional advantage is that the solution subcooling in the reservoir need not be as large as normally required. This saves duty on the refrigeration unit and also allows the solution to be handled more easily without the possibility of nucleation.

The overshoot, overshoot-shock, and continuous overshoot-shock techniques have been used interchangeably. As might be expected, there has been no dependence of growth rate on experimental method. The overshoot and overshoot-shock procedures have also been used to obtain the same type of data as that taken with the standard run method. Again, within experimental error there was no dependence of growth rate on technique employed.

3. Determination of Equilibrium Melting Temperature of a Crystal

In order to determine accurately the subcooling of the salt solutions, an experimental method was developed to find the freezing point of these solutions. By finding the temperature at which the ice crystal in solution would neither grow nor melt, and subtracting this reading from that of a growth rate run, it was possible virtually to eliminate the effect of experimental errors on subcooling determination.

For the sake of clarity, we will discuss specifically an example of our

work with 0.152% salt solution. "No-grow" experiments were performed, of course, at all the concentrations studied but the operations were similar to that described below. After the temperature of the cell coolant liquid was set near -0.1°C , the flow rate of the salt solution was set at 1 cm/sec. Then, the resultant steady state flow temperature was slightly cooler than the approximate freezing point of the solution. An ice crystal seed was then induced. As the crystal began to grow out of the capillary tube, the solution velocity was decreased slightly (by about 0.04 cm/sec) so that the temperature of the salt solution rose at a rate of approximately 0.02°C per minute. By placing the hair-line of the microscope at the leading edge of the crystal, one could observe when crystal growth ceased and melting began to occur. After the growing-melting range had been roughly determined and noted, the solution velocity was then increased slightly to a value between the original reading and the latter one. In this manner, the temperature of the salt solution very gradually decreased, but at a rate which was slower than the original one. Thus, changing the solution velocity by progressively smaller increments allowed us to achieve a very narrow temperature band within which the interface between crystal and melt did not appear to move for a period of several minutes.

The allowance of a time period of this order is necessary for the following reason. When a solid and liquid contact each other with flat interface, the melting point is a function of pressure alone and so is constant under atmospheric pressure. On a curved surface, however, the interfacial tension depresses the melting point. This melting point depression is directly proportional to γ but inversely proportional to R , the radius of curvature, and so increases as R decreases. A period of time is, therefore, required for the radius of curvature to increase to the point where it no longer affects the freezing point. Melting crystals have very blunt tips and growing ones are very sharp. The best freezing temperature is thus obtained by lowering the temperature and finding that temperature which just stops melting rather than raising it to find the point at which the crystal stops growing.

Fernandez showed that in pure water the radius of curvature of the tip of the growing dendrite so adjusts itself that 2/3 of the total subcooling is used for heat transfer and the other 1/3 is consumed by the depression due to curvature. This is a direct consequence of the maximum growth rate principle. It is thus important to be certain that the radius of curvature increases to at least 40 microns in order that the measured freezing temperature be affected by no more than 0.002°C .

Since the freezing point temperature of the 0.152% salt solution is about -0.10°C , and the thermocouple response is about $40\mu\text{V}/^{\circ}\text{C}$, the amplifier range switch is set at 0-100 μV (a multiplier of 200) with a 1 mV range card in the recorder. Under these conditions the smallest division on the calibrated chart paper corresponds to less than 0.003°C . Since the "equilibrium point" measurements are reproducible to within ± 2 divisions of the chart paper, or about $\pm 0.005^{\circ}\text{C}$, the freezing point temperature of this salt solution can be determined to within a hundredth of a degree.

The freezing point depression of NaCl solutions was also determined by reference to the literature. The data were taken from Scatchard and Prentiss (S-1), Rodebush (R-1), and Harkins and Roberts (H-4). Initially, the data from 0 to 1% NaCl were fitted with a straight line through the origin by least squares. The results yielded

$$T_F = 0.5952W$$

where T_F is the freezing point of the salt solution, and W is the weight per cent NaCl solution. Next, the deviations of all data points (0-10%) from this line were calculated. The straight line with slope 0.5952 approximated the freezing point data to within 0.002°C in the range $W = 0 - 1\%$, and to within 0.004°C for $W = 1.0$ to 1.5% NaCl. Above $W = 1.0\%$, however, the values of the deviations from the straight line first became negative, falling to -0.007°C at 2.2% , and then increased quadratically to $+0.50^\circ\text{C}$ at 9.5% NaCl. By least squares analysis, a polynomial of the second degree was fitted to the deviations above $W = 1\%$ NaCl yielding

$$T_F = 0.0366 + 0.5551W + 0.00917W^2$$

This equation described the data to within 0.006°C from $W = 1.5 - 5.5$, and to within approximately 0.020°C from $W = 5.5 - 10$.

The analysis of the freezing point data of NaCl solutions thus yielded:

$$W < 1.5 \quad T_F = 0.5952W \quad (15)$$

$$1.5 \leq W \leq 10 \quad T_F = 0.0366 + 0.5551W + 0.00917W^2 \quad (16)$$

From this analysis the value of the freezing point of a 0.152% NaCl solution is $-0.091 \pm 0.002^\circ\text{C}$. The final freezing point value determined by our "no-grow" experiment is $-0.098 \pm 0.005^\circ\text{C}$, in good agreement with the literature.

In an analogous manner, experimental determinations of the equilibrium melting temperatures of an ice crystal in 1.5% glucose solution were compared to values found in the literature (H-9,M-5), again with excellent agreement.

Our work in glucose solution will be discussed more fully in the presentation of results.

EXPERIMENTAL RESULTS

1. Distilled Water

The experimental data in distilled water were taken at water velocities of 0.042 , 0.11 , 0.22 , 0.50 , and 1.0 cm/sec, the subcoolings ranging from 0.08 to 0.87°C . The data are listed in Table 6 and plotted on logarithmic scales as growth rate versus applied subcooling in Figures 6 and 7.

Assuming for each water velocity a growth law of the form of Equation 1, a least squares fit yielded the results shown in Table 7. v is the growth rate in cm/sec, ΔT is the subcooling of the flowing water in $^\circ\text{C}$, and a' and n are constants. The value of n for the entire range of water velocities studied is close to $3/2$. Therefore, forcing $n = 3/2$ for each velocity and fitting the equation

$$v = a' \Delta T^{3/2}$$

gives the values of a' listed in Table 8.

Figure 8 shows the coefficient a' plotted as a function of water velocity using logarithmic coordinates. The data of Poisot and Fernandez are included for comparison. Using a relation of the form

$$a' = a''V^n \quad (17)$$

a least squares fit of the five points gives

$$n = 0.51$$

$$a'' = 0.0459$$

where V is the water velocity in cm/sec. Forcing a' to the equation $a' = aV^{1/2}$ yields $a = 0.0454$. Thus, the growth rate of the ice crystals is a function of the degree of subcooling to the $3/2$ power and of the water velocity to the $1/2$ power in excellent agreement with the previous work in this laboratory. Figure 9 shows this dependence as $v/V^{1/2}$ is plotted versus ΔT for all water velocities studied (88 data points). The least squares fit line through these points is

$$v/V^{1/2} = 0.0490 \Delta T^{1.56}$$

Forcing the exponent on ΔT to 1.50 gives:

$$v = 0.0456 V^{1/2} \Delta T^{3/2} \quad (18)$$

The coefficient above (0.0456) is slightly different from the value of the coefficient $a = 0.0454$ even though both refer to an equation forced to $V^{1/2} T^{3/2}$. This is explained by the fact that a results from an equal weight given to the series of 5 points obtained at each of the five water velocities, while the same weight was given to each of the 88 runs to obtain the value in Equation 18. The latter value then is probably a better value of the coefficient. Thus, we take:

$$a = 0.0456 = 2kA/(27\gamma T_M \rho_i L v)^{1/2} \quad (19)$$

The exponent of ΔT in the equation preceding 18 is slightly larger than the value of 1.50 because all the experimental data were assigned the same statistical weight. Since the relative error in temperature measurement increases as the subcooling decreases, it is clear that the data at relatively low degrees of subcooling should be given less weight.

2. Results: Salt Solution

In our experiments there are three independent variables (the solution velocity, V, the subcooling, ΔT , and the salt concentration, w, in weight per cent) which affect the dependent variable, v, the ice crystal linear growth rate. There are thus three ways of presenting data graphically. Experimentally, it is most convenient to hold V and w constant and to determine v as a function of ΔT as reported in Figures 6 and 7 for distilled water and in Figures 10 through 26 for solutions. Figures 28 through 30 show v versus w at constant solution velocity with subcooling as a parameter. Figures 31 through 35 show v versus V at each experimental value of salt concentration at various degrees of subcooling. Figures 28 through 35 are, therefore, cross-plots of some of the data shown in Figures 10 to 26. Original data are in Tables 9-13. In the salt solution graphs (Figures 28 through 30), the anomalous phenomenon of ice growth rate enhancement over that in distilled water is presented vividly. This result will be fully discussed in the next chapter.

Figure 27 (see Table 14) presents our data of growth rates in glucose solution. The purpose of this graph is to show that the increased growth rate effect is not solute specific, and is certainly not confined to electrolytes.

All of the raw data results were analyzed by assuming a growth law of the form of Equation 1 for each velocity and solute concentration. A least squares fit of the logarithm of the growth rate and the logarithm of the subcooling yielded the results shown in Tables 15 and 16.

Figure 36 and Figure 36A are plots of the exponent in the above equation as a function of concentration and solution velocity, respectively.

It is noted that additional data on the radius of curvature of a growing crystal versus subcooling, in NaCl solution and in distilled water, were taken but are presented later under the Discussion of Results.

DISCUSSION OF RESULTS

1. Distilled Water

Figures 6, 7 and 8 show the excellent agreement between the data and the growth rate law of Equation 2. The ratio of (growth rate)/(water velocity)^{1/2} is plotted versus the applied subcooling, ΔT , in Figure 9 and is compared with the resulting equations of both Fernandez and Poisot. Fernandez' coefficient is seen to agree almost exactly with the one calculated in this work. Poisot's coefficient, however, is about 18% lower than our value. This discrepancy is also seen in Figure 8 (a' vs V).

It is difficult to assess the reasons for this disagreement, particularly since it is relatively so large. This author has used Poisot's experimental apparatus and found that crystal growth rate could be influenced by changes in coolant flow rate to the cell. Since the temperature of the coolant was not monitored, this meant that cell temperature changes affected the growth rate. This effect, however, was not investigated for water velocities above 1 cm/sec and was found to be roughly an inverse function of water flow rate. Therefore, it is not expected to be a significant factor at the higher water velocities studied.

It should be noted that in Poisot's apparatus, not only was the coolant flow to the cell unregulated, but the glass flow tube was in direct contact with the aluminum cell block, thus helping to create possible temperature gradients.

Disregarding improbable errors such as improper measurement of water flow rate by Poisot, it is virtually impossible to pinpoint the reason for our differences. Our good agreement with Fernandez is not fully expected since he did not know the precise value of the water velocity at the crystal tip. His data were correlated with the average linear velocity in the flow tube, not taking into account the at least partially developed parabolic velocity profile. It may be somewhat fortunate, however, that his results were based on data taken at the higher water velocities where the flow field is less fully developed than at the lower velocities.

In our apparatus the design insured a fully developed laminar velocity profile. In Fernandez' apparatus the ice crystal was positioned just downstream from a flow constriction (20% area reduction) and the assumption of plug flow was reasonable but not completely accurate. Perhaps it is possible that Fernandez' errors in measuring water velocity and temperature tended to

cancel each other. As the velocity decreased, Fernandez' average linear velocity became a progressively poorer approximation to the actual one experienced by the crystal tip. But at the same time, temperature gradients in the tube were becoming significant. Although this is pure speculation, he may have measured a ΔT which was larger than the actual one, thus leading to a fairly accurate prediction of growth rate.

Our virtually identical results may be somewhat fortuitous.

In distilled water the data indicate that the ice crystal growth rate is controlled by convective heat transfer even at the lowest water velocity studied (0.042 cm/sec). These measurements must be extended to even lower velocities in order to observe a change in heat transfer mechanism.

The present work could not be extended further with any degree of confidence due to the increase in temperature gradients (axial and radial) and to extraneous crystal growth at the cell ends with decrease in velocity. We have reached the limitations of the apparatus in its current form. The cell flow tube must be immersed in a more adiabatic environment to extend this research.

It is interesting to note the difference between our raw data growth rate equation and the forced one. The least square line through the 88 data points was:

$$v = 0.0490 v^{1/2} \Delta T^{1/56}$$

By subtracting 0.01°C from all the subcooling readings, the data were fit by the forced Equation 18. Thus, a value of 0.01°C may be an indication of the magnitude of the possible errors in our readings.

The primary source of our experimental errors stems from the thermocouple calibration and the axial and radial temperature gradients in the flow tube. Errors of a secondary order of magnitude may arise from such effects as the difference between the local velocity to the crystal and the exact centerline velocity, calibration of the flowmeter, and the effects of air saturation and pressure head on the freezing point of water.

We can estimate the possible errors in ΔT due to a 5 foot head of water and to dissolved air. The solubilities of O_2 and N_2 at 0°C and 1 atm. of air are:

$$O_2 = 14.7 \text{ ppm.} = 0.46 \text{ millimoles/liter}$$

$$N_2 = 23.3 \text{ ppm.} = 0.83 \text{ millimoles/liter}$$

$$\text{Total } 1.29 \times 10^{-3} \text{ gm-moles/1000 gms. H}_2\text{O}$$

Therefore, the maximum possible ΔT depression due to air is about 0.002°C or $(1.86)(1.29 \times 10^{-3})$. More probably the error is about 1/10 this value since the ice bath is saturated with air and the subcooled water is agitated for a long time under air. The error due to a 5 foot water head is about 0.001°C.

2. NaCl Solution Data: Qualitative Observations

As we have seen, Fernandez' model of convective heat transfer control of the growth rate completely explains our growth observations in distilled water. His model for ice growth in salt solutions, however, adds the diffusional resistance of salt but does not fit the data, particularly at the low concentrations.

The heat and mass transfer analysis predicts a monotonically decreasing growth rate with increasing salt concentration for all subcoolings and solution velocities as shown in Figures 28, 29, and 30. In these graphs, the salt enhancement effect is seen to be greatest at the largest subcooling and the lowest solution velocity studied, $V = 0.20$ cm/sec. As seen in Figure 30, the largest observed increase in growth rate over that in pure water is about 100% at $\Delta T = 0.70^\circ\text{C}$, and 0.5% NaCl concentration. In Figure 29 ($V = 0.85$ cm/sec), the maximum enhancement occurs in the same range of ΔT and w but is only 57% above the distilled water value. In Figure 28 ($V = 3.88$ cm/sec), only a 20% increase is observed. Thus, the increase in growth rate between distilled and salt water is most pronounced at low velocities and relatively high subcoolings, but tends to disappear at $V = 3.88$ cm/sec.

The "dampening out" of the enhancement can perhaps be more readily seen in Figures 31 through 35 where growth rate is plotted versus solution velocity.

It is notable that at 6% NaCl (Figure 35) no accelerated growth rate over the distilled water value is observed, but the general character of the data remains the same as at the other salt concentrations. It is quite remarkable that at $V = 0.20$ cm/sec, $\Delta T = 0.70^\circ\text{C}$, the observed growth rate is nearly equal to the value it would have in distilled water. It appears that an enhancement might be achieved at this subcooling with a further decrease in solution velocity even at this high salt concentration.

Figures 28, 29, and 30 also show that as the subcooling is decreased and the salt concentration increased the crystal growth rate appears to approach Fernandez' predicted line. It seems that salt diffusion may become rate controlling as the concentration increases. It should be noted that in Figure 28 ($V = 3.88$ cm/sec), for example, the data point at $\Delta T = 0.10^\circ\text{C}$, $w = 6\%$ may appear deceptively high in relation to the heat and mass transfer (dashed) line. A change in subcooling of 0.01°C would make the data point coincide with the dashed line. At $w = 6\%$, we can determine the subcooling to within 0.02°C at best. At $\Delta T = 0.70^\circ\text{C}$, $w = 6\%$, however, a 0.01°C error would not change the data point from its present position and the vertical distance between the data line and the predicted line is more significant. At lower solution concentrations ($< 2\%$) the subcooling can be determined more accurately than at $w = 6\%$, generally to within about 0.01°C . This is possible because at lower concentrations we could operate the recorder amplifier at a lower scale factor. This had a two-fold effect. Not only was each division on the recorder chart paper equal to a smaller fraction of a degree (and, therefore, more accurately read), but temperature changes with time in the flowing solution could be more easily observed. Since temperature gradients are an anathema to accurate growth rate measurements, this is a very important consideration.

Note that as the solution velocity decreases the growth rate maximum becomes much broader for a given degree of subcooling.

Figure 36 reveals that as the solution velocity is decreased the dependence of growth rate on ΔT increases in about the same proportions once the concentration is above 0.5% NaCl. At 6% NaCl the exponent on ΔT is about 2 for the lower solution velocities, virtually the same dependence on ΔT as found in quiescent solution. Figure 36A plots the same information, this time employing concentration as the parameter, showing n versus solution velocity.

This graph shows that at the velocity $V = 3.88$ cm/sec the exponent averages about $3/2$ for all concentrations. As the velocity decreases and the concentration increases, the exponent becomes larger.

3. Anomalous Growth Behavior

Under certain experimental conditions two different growth rates occurred during the same run. At the solution velocity of 3.88 cm/sec and concentrations of 0.152% and 1.97% NaCl, anomalous growth behavior appeared as shown in Figure 37. The figure is in the form of a time lapse drawing, with time progressing from the left to the right. Each row represents growth at a different degree of subcooling, the bottom row being at the highest subcooling.

The diagram illustrates the fact that one growth rate is up to 40% faster than the other (assuming about a 45 degree angle between crystal axes). This is true even though the faster growing crystal tip is experiencing a slightly different solution velocity. The difference between the local velocity "seen" by the crystal growing at an angle and the velocity past the slower moving crystal can be estimated as follows. Let us assume that the slower crystal axis coincides with the flow tube axis.

$$\frac{v_{\max} - v}{v_{\max}} = \left(\frac{r'}{R'}\right)^2$$

where

R' = glass flow tube radius = 6.35 mm

r' = maximum distance between flow tube axis (slower crystal) and tip of faster growing crystal = 3/4 mm

Approximately then, the local velocity to the faster growing crystal is within 1.5% of the value to the slower crystal.

This type of growth appeared during about half of the runs employing the above-mentioned experimental parameters. It is not known why this problem arose only under these circumstances. It is interesting that the faster growth rate was found to coincide with the growth rate of a standard single crystal growing with its axis parallel to that of the capillary axis. Thus, the faster growth rate was certainly not random. The faster crystal tended to eventually overtake and obliterate the slower one as indicated in the figure.

Perhaps the most fascinating aspect of this growth anomaly lies in its apparent violation of the maximum velocity criterion. Although this principle has not been explicitly demonstrated, it has generally proved useful in predicting crystal growth rates in quiescent solution. For example, Temkin (T-2), Bolling and Tiller (B-3), and Kotler and Tarshis (K-7, K-8, K-9) have obtained good agreement with experimental data after adjusting the values of γ , the interfacial solid-liquid tension, and μ , the kinetic coefficient.

Hamilton and Seidensticker (H-2) grew germanium dendrites containing two twin planes and compared their results with an analysis based on the maximum velocity principle. Tip radii were measured, and the tips were found to have parabolic cross sections. However, the authors state that "All the dendrites observed appear to grow under the condition that the magnitude of the tip radii is determined by the presence and spacing of the twins, and not under the condition of maximum velocity". Any general conclusions to be drawn from their results would have to be tempered by the fact that the twin planes affected their kinetics and, therefore, would serve to complicate a comparison with our work.

To reiterate, the fact that we can experience two different growth rates at the same solution velocity and subcooling points out that there are operating

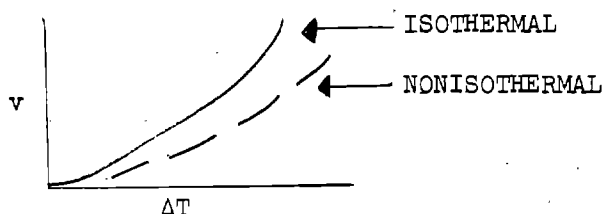
conditions under which one unique crystal growth rate is not the only possibility in the ice-water-NaCl system. The raw data graphs for conditions at $V = 3.88$ cm/sec, 0.152% NaCl and 1.97% NaCl (Figures 12 and 21) represent time asymptotic values of growth rate as a function of subcooling. The slower growth rates were discussed in reference to this anomalous behavior but were not recorded. On several occasions the faster growth rate was recorded when the angle at which the crystal was proceeding could be well approximated. These values agreed well with the "straight growth" single crystal as previously mentioned.

It is noted that Equation 10, derived before the maximum velocity criterion is applied, shows that v may have any value less than that predicted from Equation 13 and may depend on the radius of curvature, R , as well as ΔT and V .

4. A Speculation on Enhanced Ice Growth in Solution

Tiller (T-4) has suggested that for the case of no interface adsorption and no interface potential effects, straightforward partitioning of solute at the interface may produce the observed enhancement of crystal growth rates in dilute solutions. His explanation requires that in pure water the ice be nonisothermal. The cause of the temperature gradients in the ice is due to the decreasing curvature as one moves away from the tip. Thus, the interface temperature must increase also as we get farther from the tip. Then, the heat convected away through the water is the sum of that due to growth at the tip plus that conducted to it through the ice. Nonisothermal growth, then, is slower than isothermal growth due to the additional local heat flux in the solid.

In quiescent liquid one could calculate, in principle, the tip growth rate versus subcooling relationship for a paraboloid of revolution for both an isothermal and a nonisothermal interface. The resulting plot would look like that shown below.

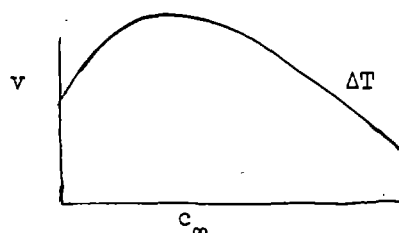


Note that according to Tiller's ideas, if the ice conduction could be reduced, the ice growth rate would increase. He postulates that the addition of solute in relatively small amounts does exactly this. That is, small solute additions serve to reduce the temperature gradients, thus creating a more isothermal interface. This would result in an increased crystal velocity as shown in the plot.

When small solute additions are made, the salt build-up at the growing interface is non-uniform for similar reasons as for the nonisothermal interface. In other words, the rejection of solute at the very tip is greater than along the sides. This solute variation decreases the tip temperature gradients by cancelling some of the local subcooling in proportion to the amount of solute present at that point along the interface. Thus, the dendrite can grow faster because part of the above-mentioned additional heat flux has been cancelled. For this argument to be effective the additional salt resistance at the tip must be more than compensated for by the decreased heat flux due to reduction of gradients in the ice.

As we slowly increase the bulk solute concentration, a greater fraction

of the total driving force is consumed by the solute build-up at the tip. A point is reached where almost all the temperature gradients have been eliminated (maximum growth rate). The continued addition of solute will then begin to decrease the growth rate and the resulting plot of growth rate versus bulk solute concentration for a given ΔT would be as shown below.



5. Isothermal Versus Nonisothermal Ice Crystals Growing in Pure Water

Fernandez, we recall, assumed that the heat taken away from the ice through the water at the tip is due solely to the growth of ice at the tip (latent heat). This assumes the ice to be isothermal and has given good results in pure water thus far. The ice we know to have temperature gradients in it because of the varying curvature over its surface, but the question arises as to whether the additional local heat flux at the tip caused by these gradients in the solid is important or not.

Using the assumption of a nonisothermal interface, Kotler and Tarshis (K-7, K-8, K-9) have calculated the tip ice growth rate as a function of bath subcooling in the range of -2°C to -6.5°C in pure, quiescent water. Their results are in excellent agreement with the experiments of Lindenmeyer when γ and μ were adjusted to 20 ergs/cm² and 16 cm/sec $^{\circ}\text{C}$, respectively, which are about 50 to 60% of the experimental values.

They also calculated the relative heat fluxes in the solid and liquid at the dendrite tip using the above values of γ and μ for nonisothermal growth. Results indicated that the flux in the solid is approximately one-third of that in the liquid for growth in quiescent, pure melt in the above reported temperature range. According to their analysis, nonisothermality in the solid was shown to have an important effect on growth rate.

Thus, we have two different results which may not be paradoxical necessarily since Fernandez' analysis obviously is invalid in quiescent water, as noted previously. (The heat flux in the solid may play an important role in crystal growth, as Kotler and Tarshis believe, but perhaps becomes a more important factor as the solution velocity goes to zero.)

True comparison of the convective heat analysis of Fernandez with the diffusive heat transfer analysis of Kotler and Tarshis is not applicable, of course. The main point is, however, that we cannot dismiss the potential importance of the role of nonisothermal ice, particularly at low solution velocities.

6. Applicability of Tiller's Postulate to Ice Growth in Solution

Kotler (K-6) (a student of Tiller) has recently attempted a mathematical analysis of nonisothermal, non-isococoncentrate dendrite growth in binary systems with only meager success. In attempting to predict the ice-water-KCl data of

Lindenmeyer using the considerations put forth in the previous several paragraphs, Kotler's results were substantially below the experimental values. The predicted value of the maximum growth rate was correctly calculated to occur at a bulk concentration of about 0.1 mole/liter but was only 1% above the pure water growth rate. This compares with an experimental enhancement of about 30% under the same conditions. No error has been found in Kotler's work which might explain these discrepancies. A footnote in Kotler's thesis promises that a more rigorous attempt at the solution of the solute problem was already underway in 1968, but no further pertinent publications have been uncovered. Quantifying the phenomenon, therefore, is an elusive problem.

In regard to the data, there are certain qualitatively satisfying aspects of Tiller and Kotler's work which should be mentioned. First, their theory is not solute-type specific. It applies to glucose as well as to salts, and it applies to chlorides just as well as fluorides, for example.

Secondly, one would expect that, for a given concentration in the range of the growth rate maximum and for a specific solution velocity, an increase in subcooling may yield a greater growth rate enhancement. This may be explained, according to Tiller's theory, by the fact that the larger applied subcooling leads to greater solute rejection at the tip (due to a larger overall driving force), and thus a higher degree of non-uniform concentration at the interface. As previously noted, this may lead to a reduction of the temperature gradients making the interface more isothermal and yielding a more enhanced growth rate. Also, as the subcooling becomes greater, the radius at the tip becomes smaller and the temperature gradients in the ice are larger. Since a greater heat flux in the solid exists, a larger increase in growth rate is possible by reducing this conduction. Perhaps this is more important than the previous factor.

For a given solute concentration and subcooling, an increase in solution velocity should serve to dampen the enhancement effect by removing the rejected salt from the vicinity of the interface. This is what we observe experimentally.

Lastly, this explanation is based on heat and mass flux considerations, not kinetics. All of the crystal growth work done in this laboratory (P-1, F-2, F-3, F-4) has shown that kinetic resistance is negligible compared with heat resistance even at high solution velocities.

Our data, then, seem to substantiate these admittedly gross speculations. Thus, Tiller's theory cannot easily be dismissed as yet.

Terwilliger and Dizio (T-3) performed experiments and analyzed mathematically the one-dimensional (planar) growth rate of ice in water and dilute salt solutions. The heat of solidification was withdrawn through the ice. They accounted for both heat and salt transport. Fixed micro-conductance probes were employed to monitor experimentally the NaCl boundary layer ahead of the growing interface and their data agree well with theory.

For the solute distribution in the liquid they give:

$$\frac{c - c_{\infty}}{c_i - c_{\infty}} = e^{-\frac{(Z/D)(\rho_i/\rho_L)(X-\delta)}{\delta}} \quad (20)$$

where δ is the interface position, cm, Z is the solidification rate parameter, cm^2/sec , D is the salt diffusion coefficient, cm^2/sec , and c is the concentration at point X .

Now, $\frac{Z}{\delta} = \frac{d\delta}{dt} = v$, the freezing rate, since $\delta = \sqrt{2Zt}$ from their heat transfer analysis.

Then,

$$\frac{c - c_{\infty}}{c_i - c_{\infty}} = e^{-(v/D)(\rho_i/\rho_L)(X-\delta)} \quad (21)$$

$$\ln \frac{c - c_{\infty}}{c_i - c_{\infty}} = -\frac{v}{D} (\rho_i/\rho_L)(X-\delta) \quad (22)$$

$$-\frac{D}{(\rho_i/\rho_L)(X-\delta)} \ln \frac{c - c_{\infty}}{c_i - c_{\infty}} = v \quad (23)$$

We note that for a particular freezing rate and constant $D/(\rho_i/\rho_L)$, a unique boundary layer thickness is predicted in the absence of forced convection. Differentiating the above equation,

$$\frac{dv}{dc} = -\frac{D}{(\rho_i/\rho_L)(X-\delta)} \frac{1}{c - c_{\infty}} \quad (24)$$

Since

$$c = c_i, \quad X = \delta$$

and

$$c \rightarrow c_{\infty} \text{ as } X \rightarrow \infty$$

we can see that a plot of ice growth rate versus concentration of solute in bulk solution (at fixed solution velocity and subcooling) yields a monotonically decreasing function. The slope is never positive since $c \geq c_{\infty}$ due to solute rejection at the interface, and $X \geq \delta$ due to the coordinate system chosen.

This result is in qualitative accord with Fernandez' predicted function of growth rate versus concentration (Figures 28 through 31).

For a planar crystal morphology both theory and experiment show that no unexpected (that is, enhanced) growth rates occur in salt solution. The system behaves exactly as predicted by heat and mass transfer calculations, i.e., any increase in salt concentration invariably leads to slower growth rates.

Moreover, the experimental concentration interval ranged from 0.005 to 0.10 molar (0.03 to 0.6 wt.% NaCl) and thus covers the range where rate enhancement has been observed in dendrite growth.

This evidence leads us to expect that growth rate enhancement of dendrites in salt solution is related to tip curvature in some manner.

In a communication, Probstein (P-2) has suggested that the anomalous increase in growth rate which we observed might be caused by the effect of free-stream turbulence on the rate of heat transfer. Kestin (K-2) points out that the intensity of turbulence exerts a local effect on the rate of heat transfer (e.g., increases it) which is most pronounced near the stagnation point of a cylinder. The reasons for this effect are currently unknown. It must be

remembered, though, that the enhancement effect is most pronounced as the solution velocity goes to zero. Therefore, it is not likely that any free-stream effect is responsible for the anomaly. All our experiments were conducted under fully developed pure laminar flow.

7. Ice-Water Surface Tension

a. Distilled Water

We have seen that the Fernandez model describing the ice growth rate mechanism leads to the growth law of Equation 13. Therefore, a figure for the interfacial surface tension can be computed.

Rearranging Equation 13 and inserting the values of the properties at 0°C taken from page 100 of (F-2), we get:

$$\gamma a^2 = \frac{4k^2 A^2}{27 T_{M^0}^3 L_v} = 1.6425 \times 10^{-9} \text{ cal./}(\text{sec.cm}^3 \text{K}^3) \\ = 6.874 \times 10^{-2} \text{ ergs/}(\text{sec.cm}^3 \text{K}^3)$$

The symbol A above is the same as Fernandez $\Pi_T'(0, Pr, 0)$ and has the dimensionless value 1.48 at 0°C.

Using our value of $a = 0.0456$, γ is calculated as 33.2 ergs/cm². This agrees quite well with Fernandez' value of 31.8 ergs/cm² using $a = 0.0466$, but is lower than Poisot's result of 49.3 ergs/cm² with $a = 0.0374$. Recently, however, Ketcham and Hobbs (K-3) have determined γ by a direct experimental technique and have reported $\gamma = 33 \pm 3$ erg/cm² at 0°C in excellent agreement with our work.

The only other direct technique for measuring this value has been reported by Jones and Chadwick (J-4). Their results were found by observing the shapes of grain-boundary grooves at the interface. A value of $\gamma = 41 \pm 9$ erg/cm² was derived in satisfactory agreement with our figure of 33 ± 4 erg/cm².

Other workers have attempted to determine the ice-water surface tension using different techniques such as applying Turnbull and Fisher's (T-8) theory of homogeneous nucleation to the freezing of water droplets. Dufour and Defay (D-1), for example, report theoretical estimates ranging from 10 to 49 ergs/cm², but no actual ice crystal growth rate measurements are cited there. Hobbs and Ketcham (H-7) have noted that values of γ determined from homogeneous nucleation theory are not very accurate and that by a judicious and yet quite reasonable choice of parameters, the ice-water surface tension can be determined as $\gamma = 32$ ergs/cm² as also calculated by Turnbull (T-7).

Mason (M-3) concluded that $12 < \gamma < 22$ ergs/cm² and Dufour and Defay determined that $\gamma = 20.24$ ergs/cm² by using homogeneous nucleation data. Also, Fletcher (F-6) theoretically predicted $\gamma = 20$ ergs/cm² by employing entropy considerations. These values are most likely not very accurate, however, due to the inherent uncertainties in estimating the parameters, and uncertainty in the models used.

Ketcham and Hobbs' experiments have been criticized in a very recent paper by Knight (K-5). However, no actual errors could be pinpointed by Knight with any certainty. It seems reasonable to assume that Ketcham and Hobb's work is valid until either obvious problems are discovered or an

improved determination is made. Thus, the experimental values of Ketcham and Hobbs and of Jones and Chadwick must be considered as the most reliable to date outside of our work with which both agree.

b. Solutions

Jones and Chadwick (J-3) also have measured ice-solution interfacial energies for the ice-water-sodium chloride system using the same technique as they did for pure water. Determinations were made for salt concentrations from 0 to 1.0 M (0 to 5.5 wt.% NaCl). The interfacial tension seemed to increase linearly with solute concentration, its value at about 6% NaCl being approximately 13 erg/cm² greater than in pure water. The data were quite scattered, however.

In an analysis of morphological stability of ice growth in aqueous solution, Hardy and Coriell (H-3) have found that various solutes at a concentration of 10⁻³ M had no effect on the surface tension, which they reported as 22 ergs/cm² in distilled water. NaF was the only exception, as γ decreased about 15% when the subcooling was increased from 0.12 to 0.19°C. No explanation was advanced for this result. A solution of 0.1 M HCl was reported to have no effect on the surface tension.

These papers seem to indicate that nothing magic happens to the value of the ice-water surface tension upon the addition of a solute. Salts and sugars tend to raise the surface tension.

8. The Radius of Curvature of a Growing Crystal

In order to test fully the validity of Fernandez' growth equations as well as to derive fundamental data about the actual magnitude of the radius of curvature and its functional relationship with temperature, direct measurements of the crystal tip radius were undertaken.

As an ice crystal grew out of the capillary tube into the flowing stream under representative run conditions, the seed holder was rotated to expose the edge view of the growing ice. A photograph of the tip region was taken as the solution velocity and temperature were recorded. Data were taken both in distilled water and in 0.15% NaCl solution and are plotted in Figures 38 and 39, respectively. The subcooling range was 0.1 to 0.6°C. See Table 17. The velocity ranged from 0.4 to 0.9 cm/sec, with no observable dependence of radius of curvature on velocity in this narrow range.

Each roll of film was calibrated by photographing the glass capillary tube and then comparing the width measurement on the picture with the actual width of the tube as determined by a micrometer. The magnification was found to be 100 power. Photographs of the edge views of four growing crystals are shown in Figure 40, and the top view of a crystal is shown in Figure 41 to demonstrate the typical morphological character of the ice.

Photographs such as those shown in Figure 40 were used to estimate the radius of curvature of the tip in the following way. The shape of the tip was approximated by a parabola. The radius of curvature, R , was then calculated by using the equation

$$R = \frac{w^2}{8l}$$

where w is the width of the crystal at a distance l from the tip. Several measurements of w and l were taken on each photograph and an average value of R

was found. The average and range are shown in the figures.

Figures 38 and 39 make several things apparent. First, the tip radius of curvature is inversely related to the applied subcooling. This is most obvious in distilled water (Figure 38), where the indicated data line is drawn exactly proportional to the inverse of the subcooling (slope = -1) and is an excellent fit. The line drawn for the salt data exhibits the same general effect but is somewhat steeper (slope = -1.5). Thus, Figure 39 shows that the radius of curvature in NaCl solution apparently decreases more rapidly than in distilled water as the subcooling increases. A decrease in radius of curvature increases the heat transfer coefficient at the tip invariably (by any heat transfer theory). But as the radius at the tip becomes smaller, the temperature gradients in the ice are larger.

(Note, by Tiller's analysis, that since a greater heat flux in the solid exists at smaller R, a larger increase in growth rate is possible by reducing this conduction via added solute.)

Also, note that according to Fernandez' theory, a change in radius of curvature cannot lead to growth enhancement. By his theory the unique radius of curvature is chosen which maximizes the growth rate. Any other value of R would yield a slower growth rate.

It seems worthwhile, then, to compare the growth rates in distilled and in salt water with their respective radii of curvature for the same subcooling. At $\Delta T = 0.5^\circ\text{C}$, for example, the tip radius of curvature in distilled water is about 1/3 larger than in 0.15% NaCl solution. Interestingly, the growth rate data at $V = 0.20$ and 0.85 cm/sec, 0.15% NaCl (Figures 10 and 11), show about a 1/3 increase in growth rate in NaCl solution at $\Delta T = 0.5^\circ\text{C}$ over the pure water value. At $\Delta T = 0.2^\circ\text{C}$, where both values of R are approximately equal, the data shows virtually no growth rate enhancement. Below $\Delta T = 0.15^\circ\text{C}$, the radius of curvature data are not very complete.

We cannot attribute any great degree of accuracy to the radius of curvature data. Comparisons between the relative values of R in distilled water and NaCl solution are most probably tenuous at best. The trend of the data indicate that just a small solute addition may change the radius of curvature as well as the growth rate. The result, although admittedly tentative, points to an increased growth rate accompanied by a decreased radius of curvature (relative to pure water). This observation violates Fernandez' theory and leads us to suspect that growth rate enhancement and radius of curvature are perhaps interdependent.

It is clear, though, that our data in Figures 38 and 39 do not agree with the values predicted by Fernandez' theory, and indeed, are much greater. In pure water the experimental radii are 6.5 times those calculated from Equation (11). In obtaining our radius data, the ice crystal was rotated into position to show the edge view as explained above. Care was then taken, however, to tilt the crystal a few degrees in each direction in order to judge the position of minimum width. Only then was a photograph taken. Therefore, it is unlikely that the observed discrepancy is due to carelessness in photographing the crystal.

The only other experimental determinations of ice crystal radius of curvature data are those of Ryan in 1969. His results indicate the same general behavior as ours: R decreases with an increase in supercooling. Quantitatively, however, his values are much greater than ours, ranging from $R = 160$ microns at $\Delta T = 0.2^\circ\text{C}$ to 30 microns at 1.5°C . Since he also approximated the shape of the crystal tip by a parabola and thus employed the same equation to calculate R,

one would expect closer agreement between his work and ours in distilled water. It is possible that Ryan was unable to rotate the growing crystal under a microscope to find the position of minimum width and thus estimated quite large values of R . If the crystal is at only a slight angle from true vertical, the apparent crystal thickness is easily doubled, thus multiplying the tip radius of curvature by a factor of 4. Ryan does not explain his experimental method for determining R so it is difficult to pinpoint any inadequacies which would cause a disagreement by a factor of 50 or so. It should also be noted that his data exhibit a great degree of scatter.

The poor agreement between our data and the values of R predicted by Fernandez is apparent in Figures 38 and 39. The only adjustable parameter in his equation for R is γ , the interfacial tension. In order to fit the data, γ would have to be on the order of 300 ergs/cm^2 , a value which is incredibly high. There is no obvious way to reconcile Fernandez' equation with the data taken for this thesis.

It is surprising that the disagreement is so severe. Fernandez' work correctly predicted the growth rate of ice crystals at subcoolings below 1.0°C for distilled water velocities from 0.04 to 46 cm/sec. This, of course, included the prediction that the growth rate, v , is proportional to the $3/2$ power of the applied subcooling and to the $1/2$ power of the flow velocity in distilled water. Even the calculated value of the ice-water interfacial tension estimated by Fernandez' analysis is very reasonable.

Among the factors possibly responsible for our differences could be that our approximation of a parabolic cross section of a growing ice crystal is poor. By inspecting the photographs in Figure 40, however, we can see that any errors incurred by invoking this assumption would seem to be minimal. Particularly at the lower subcoolings the shape seems to deviate from a true parabola, but it is not apparent that this would lead to errors of such a great magnitude.

Perhaps a more serious consideration is whether Fernandez' theoretical analysis is valid. Particularly germane to this discussion are Harriott's comments in a personal communication sent last year (H-5). He pointed out that Fernandez used boundary layer theory to predict the heat flux, thus assuming the boundary layer to be thin compared to the radius of curvature of the tip. However, both the growth rate data and the theory show that the boundary layer thickness is at least equal to the radius of curvature in some instances, and greater than the radius of curvature under most conditions.

In attempting to explain the anomalous growth in dilute salt solutions he stated:

..."Perhaps the actual radius of curvature of the crystal tip is much greater than the theory predicts but varies with salt concentration in such a way as to make the apparent growth rate increase with salt concentration...the smaller radius [IN SALT] could offset the loss in driving force caused by salt diffusion and give a higher growth rate." (Brackets mine)

We have already mentioned why the actual radius of curvature was postulated to be greater than the predicted one and shall investigate this thought in more detail. Under specified growth conditions, Harriott estimated the boundary layer thickness to be 5 microns while Fernandez' predicted radius of curvature is about 0.2 micron. For growth conditions corresponding to an approximate boundary layer thickness of 86 microns, the predicted radius of

curvature is about 1 micron. If, indeed, these figures are representative of the actual situation, Fernandez' theoretical analysis is invalid. Substitution of some of our typical data for v , V , ΔT , and R into Fernandez' equation (before the invocation of the maximum velocity criterion) results in a negative value for γ . The equation used had the form:

$$v = \frac{kA}{\rho L v^{1/2}} v^{1/2} \left(\Delta T - \frac{\gamma T_M}{\rho L R} \right) / R^{1/2} \quad (25)$$

This points to the fact that either the analysis is incorrect or that our curvature data are not as useful as we presume.

Our experimentally determined radii of curvature do not agree with Harriott's calculations either but are in the direction indicated by him.

The second point concerning Harriott's comment is his postulate that the actual radius of curvature might vary with salt concentration. We have previously alluded to this thought, both in discussing Tiller's ideas and in regard to our own curvature data.

In order fully to test that hypothesis it would be necessary to take additional data of the type shown in Figures 38 and 39. It would be most interesting to extend the data up to higher subcoolings to determine whether the discrepancy between the radius of curvature in distilled water and in salt solution becomes greater. This is expected since the anomaly is a function of subcooling. Radius of curvature data at various salt concentrations and even with a variety of other solutes would also be useful.

Since Tiller's considerations depend on the distribution of solute at the growing interface, radius of curvature data as a function of solution velocity could be employed to show whether high velocities have an effect. High velocities serve to increase transport rates and thus decrease salt concentration gradients.

As shown in Figures 31 through 35, solution velocity does affect the growth rate data. However, as previously noted, a very limited range of velocity was used in determining the radius of curvature data in Figures 38 and 39. Thus, no observable dependence of radius of curvature on velocity was found.

9. Low Reynolds Number Heat Transfer to a Crystal Tip

To estimate the heat transfer coefficient to the stagnation line of the tip of an ice crystal at low Reynolds numbers, we have investigated heat transfer work to a circular cylinder presented in the literature. Boundary layer theory is not adequate since it does not apply at zero or very low velocity and it requires that the boundary layer be thin compared to R . We note that boundary layer theory used in Fernandez' analysis is not applicable since the boundary layer thickness is, in most cases, greater than the radius of curvature.

Hieber and Gebhart (H-6) have derived an expression for the Nusselt number at low Reynolds numbers using many of the considerations of Kaplun (K-1) and Proudman and Pearson (P-3). Based upon the temperature expansion in the Stokes region (valid near the body), the Nusselt number is derived,

$$Nu = \frac{hR}{k} = \frac{1}{\ln(8/\gamma'Pr Re)} \left\{ 1 - \frac{a_3(Pr)}{\ln(8/\gamma'Pr Re)^2} \right\} + O(\ln Re)^{-4} \quad (26)$$

$a_3(Pr)$ is a constant for a given Prandtl number and is about 4.07 for $Pr = 13.4$ (pure water at 0°C).

One problem is that while Equation (26) is valid as the Reynolds number approaches zero, we do not know how high the Reynolds number may be, nor how it connects with the solution for boundary layer flow. We leave the problem for future investigation by others.

SUMMARY AND CONCLUSIONS

Our distilled water work at low flow velocities has shown that Fernandez' equation still holds all the way down to $V = 0.42$ cm/sec for subcoolings less than 1°C . The growth rate of ice along the basal plane in subcooled water is then proportional to the $1/2$ power of the water velocity and the $3/2$ power of the subcooling. The growth rate model assumed that the factor completely controlling dendritic ice growth is the rate at which the latent heat of solidification is transferred by convection from the crystal to the flowing water. By using the growth rate equation it was possible to derive a value for the ice-water interfacial tension, γ . Our value of 33 ergs/cm² compares well with a recently reported work in the literature.

We have, for the first time, fully characterized the aspects of the observed solute anomaly. Upon the addition of NaCl, Fernandez' equation no longer holds. His heat and mass transfer analysis predicts a monotonically decreasing growth rate with increasing salt concentration for all subcoolings and solution velocities. Instead, we have observed a growth enhancement effect which is greatest at the largest subcoolings and the lowest solution velocity studied ($V = 0.20$ cm/sec). The greatest growth rate enhancement over that in pure water is about 100% at $\Delta T = 0.7^{\circ}\text{C}$ and 0.5% NaCl. The anomaly tends to disappear at the highest solution velocity studied ($V = 3.9$ cm/sec).

In the equation $v = a\Delta T^n$, n approaches $3/2$ as the solution velocity increases to $V = 3.9$ cm/sec. At $V = 0.20$ cm/sec, n is near 2 for all but the lowest solution concentration (0.15% NaCl).

When the ice crystal growth rate is plotted versus salt concentration, the growth rate maximum becomes much broader with a decrease in solution velocity for a given degree of subcooling.

The solute anomaly was also demonstrated for 1.5% glucose at a solution velocity of 0.64 cm/sec, showing that this effect is not confined to electrolytes. Under the above experimental conditions the enhancement in glucose solution was about 40% over that in distilled water at $\Delta T = 0.5^{\circ}\text{C}$.

In general, then, the growth rate versus concentration has a maximum, the anomaly is located within a dilute concentration range, the effect is not very solute specific, the maximum becomes more pronounced with increased subcooling, and the effect tends to disappear with an increase in solution velocity. No simple, concise explanation, qualitative or quantitative, has yet been advanced in the literature to describe the phenomenon completely with respect to all of the data available.

Our radius of curvature data in distilled water show an inverse relation to subcooling, but are 6.5 times greater than that predicted by Fernandez. There is no obvious way to reconcile our data with Fernandez' predictions. The radius of curvature data taken in 0.15% NaCl solution have a steeper negative slope when plotted versus subcooling and are of the same magnitude as that in distilled water. The data are somewhat scattered so that it is difficult to draw any firm conclusions concerning the relative differences between curvature in salt and pure water at this time.

But we recall that in salt water the ice crystal growth rate is, under certain conditions, much larger than in distilled water. Since the growth rate in distilled water is completely controlled by heat transfer, a faster growth rate in salt solution means higher heat transfer. The properties of dilute salt

solutions do not change enough to account for even a small portion of the necessary increased heat transfer. Therefore, a change in the radius of curvature in salt water must occur. The mechanism for this change, however, is unknown. We could only make speculations and also eliminate some of the irrational observations in the literature.

We have shown how straightforward partitioning of solute at the interface (Tiller's idea) may produce the enhancement of growth by creating a more isothermal interface. If such speculations actually hold, the radius of curvature would not only be a function of subcooling, but also a function of concentration and perhaps solution velocity to some extent. This would be a useful area for further research.

It is noted that Fernandez' equations lack some rigor on several counts. Although they are accurate for predicting the rate of ice growth in distilled water, and for calculating the ice-water interfacial tension, they are not useful for predicting growth rates in salt solution. In addition, we found that our radius of curvature data in distilled water do not fit the values predicted by Fernandez. In NaCl solution our radius of curvature data tended to differ with those in distilled water. Fernandez' equation cannot predict this. Indeed, by his theory a change in R leads to a lower growth rate. Moreover, boundary layer theory used in Fernandez' analysis is not applicable since the boundary layer thickness is at least equal to the radius of curvature and, in most cases, greater than the radius of curvature. The theory presumes the boundary layer to be thin compared to the radius of curvature. Our attempts to predict the heat transfer coefficient without boundary layer assumptions were not successful.

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NOMENCLATURE

a, a', a'', b, c'	= coefficients in growth rate law, e.g. see Eqs. 1 to 5, 14, etc.
A	= dimensionless temperature gradient at ice-water interface
c	= liquid phase solute concentration, mol/l
c_i	= interfacial solute concentration, mol/l
c_∞	= bulk liquid phase concentration, mol/l
D	= salt diffusion coefficient, cm^2/sec
h	= heat transfer coefficient, $\text{cal}/\text{cm}^2\text{-sec-}^\circ\text{C}$
k	= thermal conductivity of water or salt solutions, $\text{cal}/\text{cm-sec-}^\circ\text{C}$
L	= heat of solidification of water, cal/gm
m	= exponent on V in growth rate law
n	= exponent on ΔT in growth rate laws
Nu	= Nusselt number, hR/k
Pe	= Peclet number, $Pr \cdot Re$
Pr	= Prandtl number
q	= heat flux at ice-water interface, $\text{cal}/\text{cm}^2\text{-sec}$
r	= local radius of curvature, cm
r'	= maximum distance between flow tube axis and crystal tip, mm
R	= tip radius of curvature, cm
R'	= glass flow tube radius, mm
Re	= Reynolds number, DV/ν
t	= time, sec
T	= temperature, $^\circ\text{K}$
T_F	= freezing point of NaCl solution, $^\circ\text{C}$
T_i	= ice-water interface temperature, $^\circ\text{K}$
T_M	= ice point = 273.2°K
T_∞	= bulk temperature, $^\circ\text{K}$

NOMENCLATURE (Cont'd.)

$U(x)$	= potential velocity, cm/sec
u_x, u_y	= water or solution velocity components, cm/sec
v	= ice crystal growth rate, cm/sec
V	= water or solution velocity, cm/sec
w'	= salt mass fraction
W, w	= weight per cent NaCl in solution
x, y	= boundary layer coordinates
X	= space coordinate, cm
Z	= solidification rate parameter, $\delta(d\delta/dt)$, cm^2/sec
α	= thermal diffusivity, cm^2/sec
β	= $\gamma T_M / \rho_i L$, $\text{cm } ^\circ\text{K}$
γ	= ice-water interfacial energy, ergs/cm^2
γ'	= Euler's constant = 0.5772...
ΔT	= $T_M - T_\infty$ = applied subcooling, $^\circ\text{C}$
δ	= interface position, cm
δT	= kinetic temperature driving force, $^\circ\text{C}$
ν	= kinematic viscosity of water or solutions, cm^2/sec
ρ_i	= density of ice, gm/cm^3
ρ_L	= density of water or solution, gm/cm^3

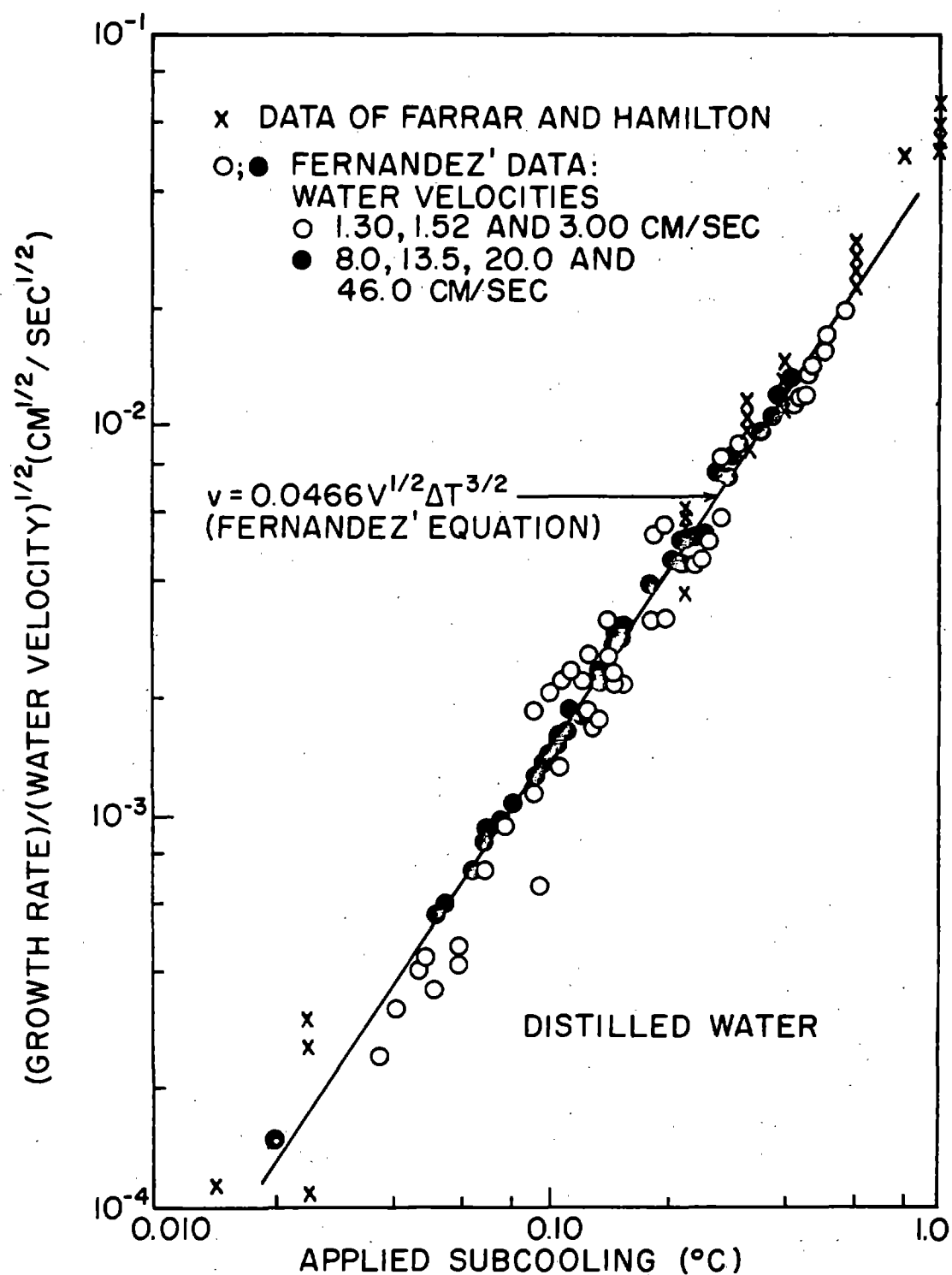


FIGURE 1 : GROWTH RATE DATA IN SUBCOOLED DISTILLED WATER COMPARED TO FERNANDEZ' EQUATION

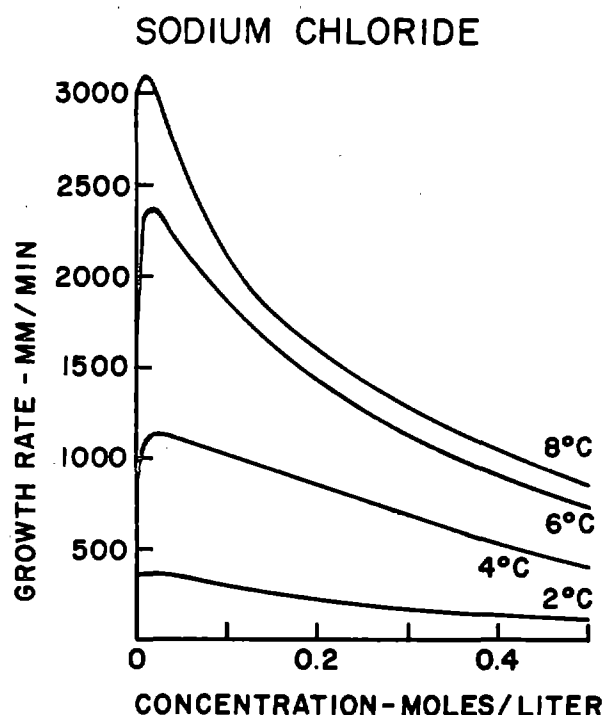
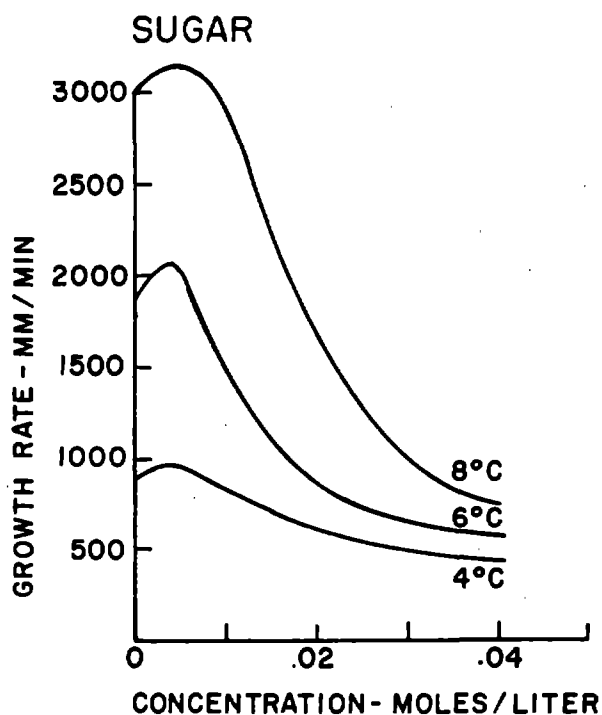
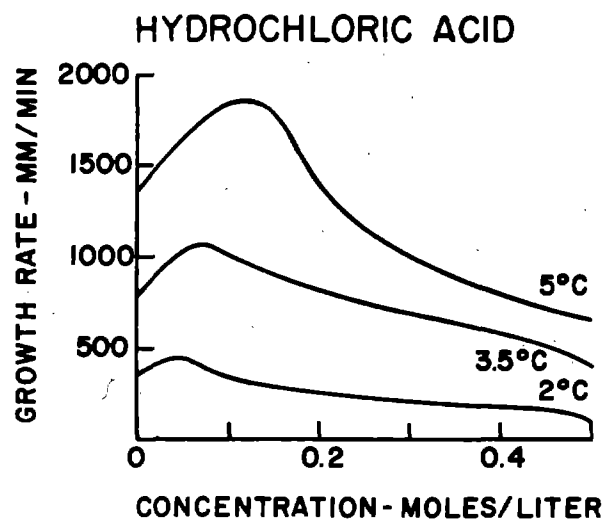
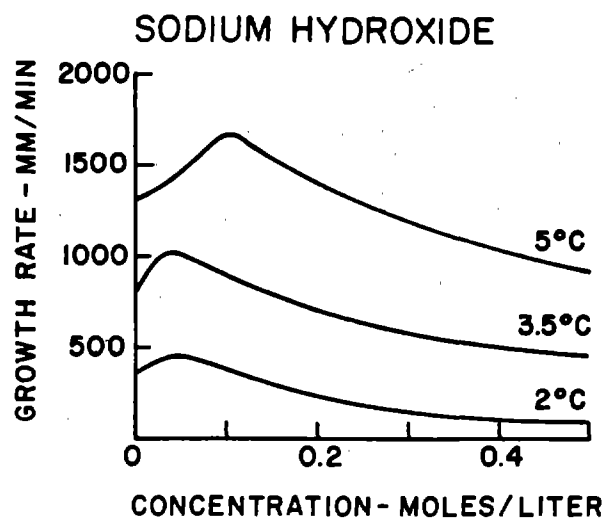


FIGURE 2 : ICE CRYSTAL GROWTH RATE IN CAPILLARIES VS. SOLUTION CONCENTRATION AS A FUNCTION OF SUBCOOLING (TAMMANN AND BUCHNER, 1935)

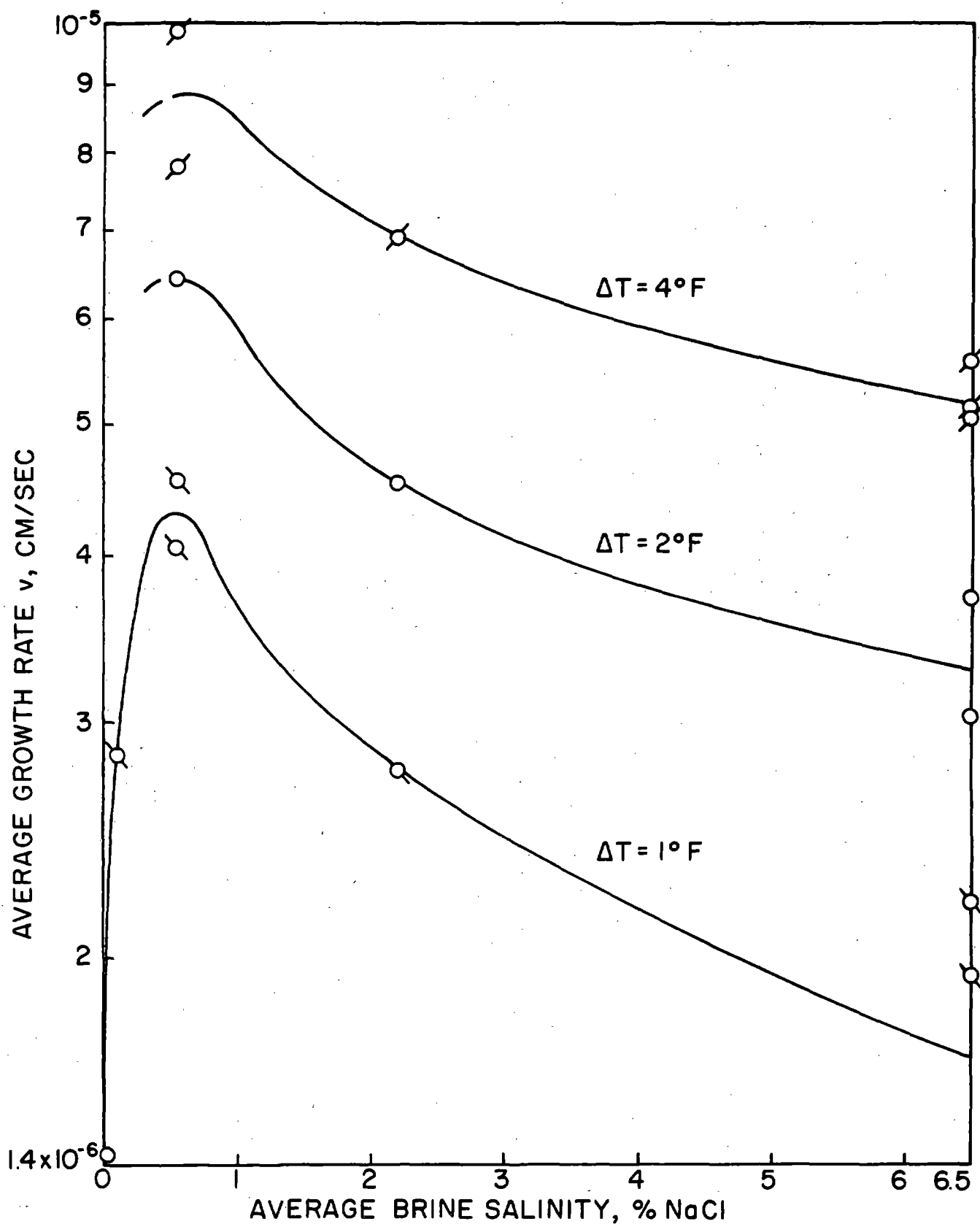


FIGURE 3

: AVERAGE ICE CRYSTAL GROWTH RATE VS. AVERAGE
BRINE SALINITY IN A DIRECT FREEZE SEPARATION
REACTOR (JOHNSON, ET AL., 1967)

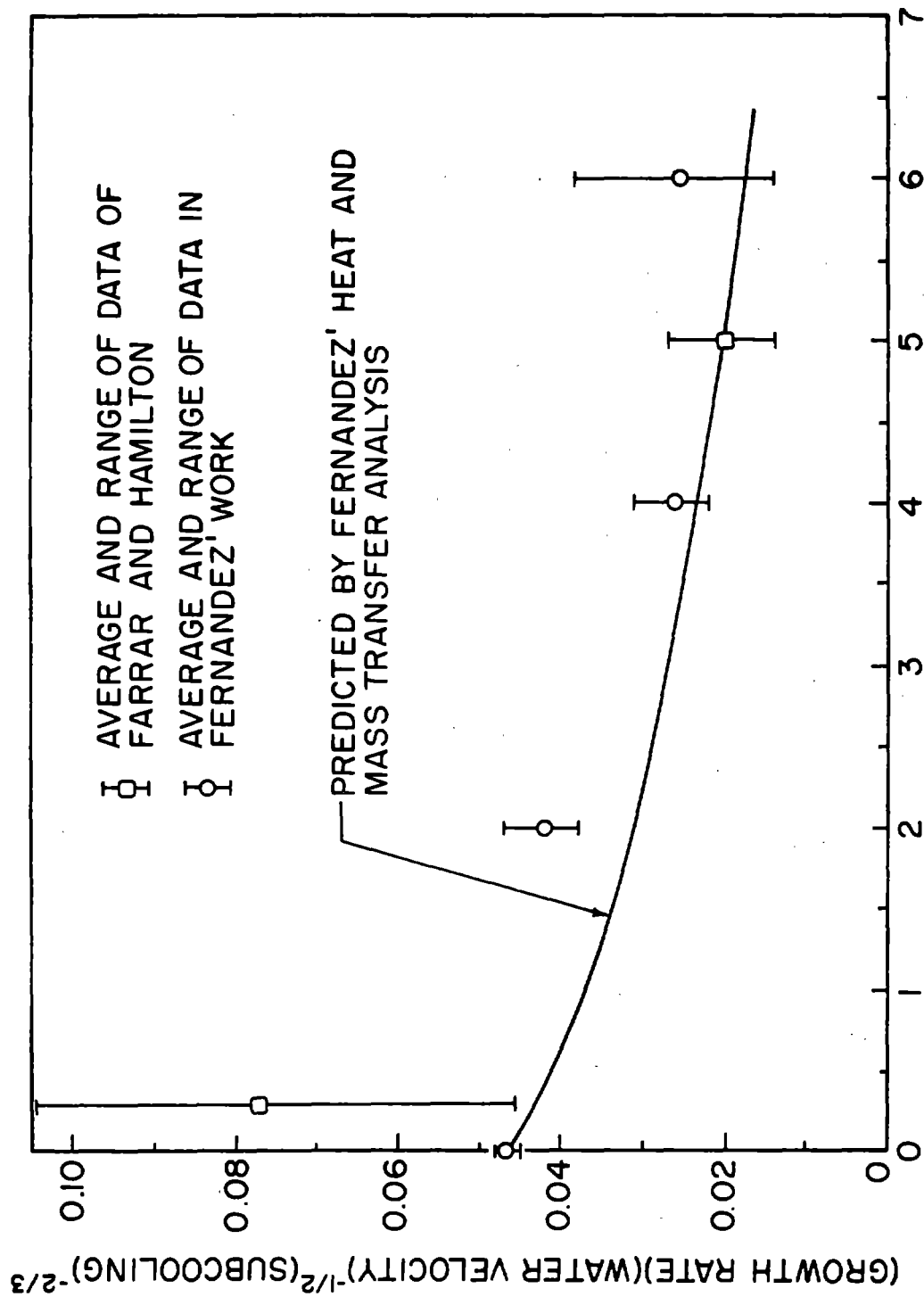


FIGURE 4 : THEORY AND EXPERIMENTS IN SALT SOLUTIONS

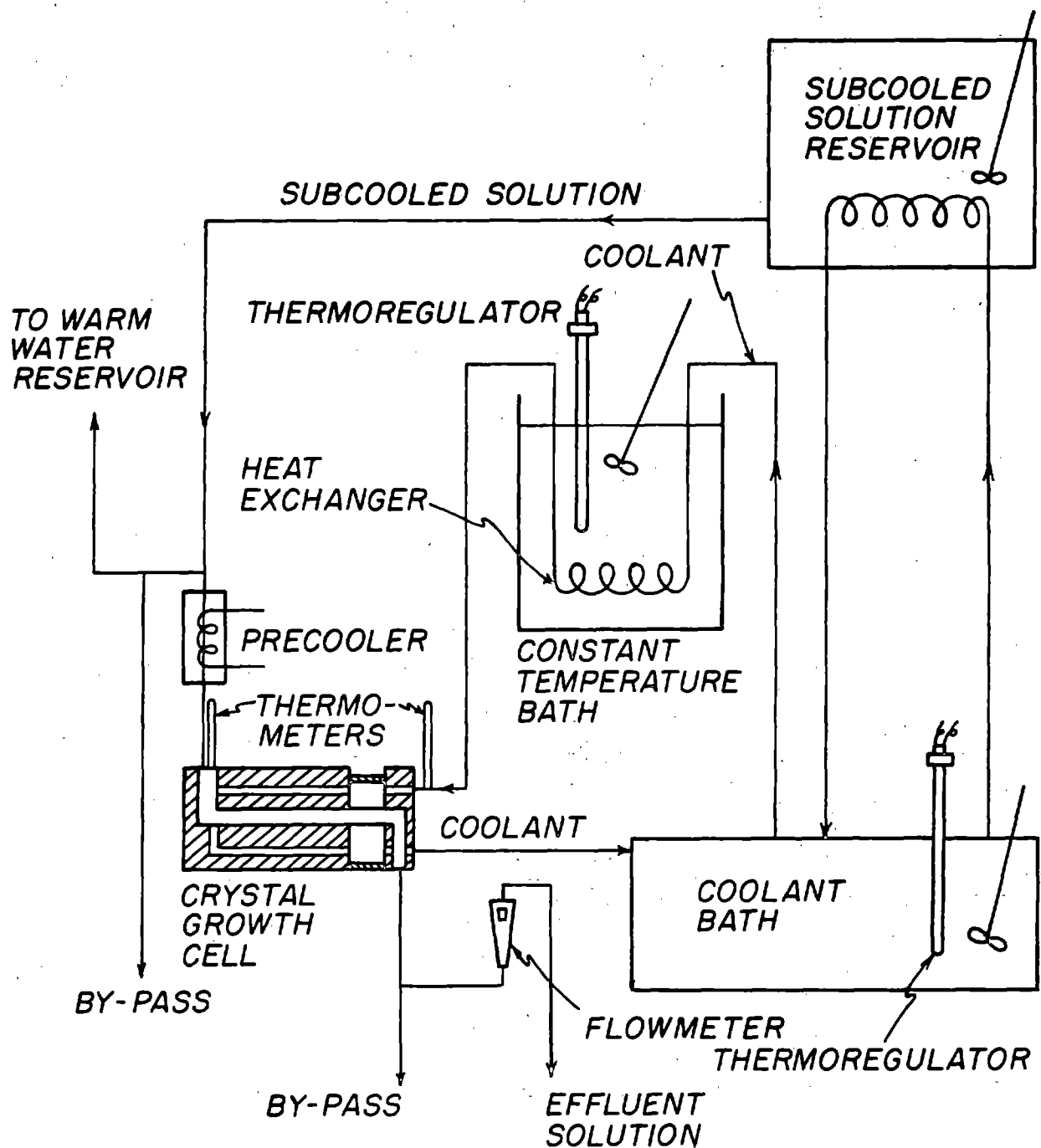


FIGURE 5A : ICE CRYSTAL GROWTH APPARATUS - DIAGRAM OF EXPERIMENTAL SET-UP

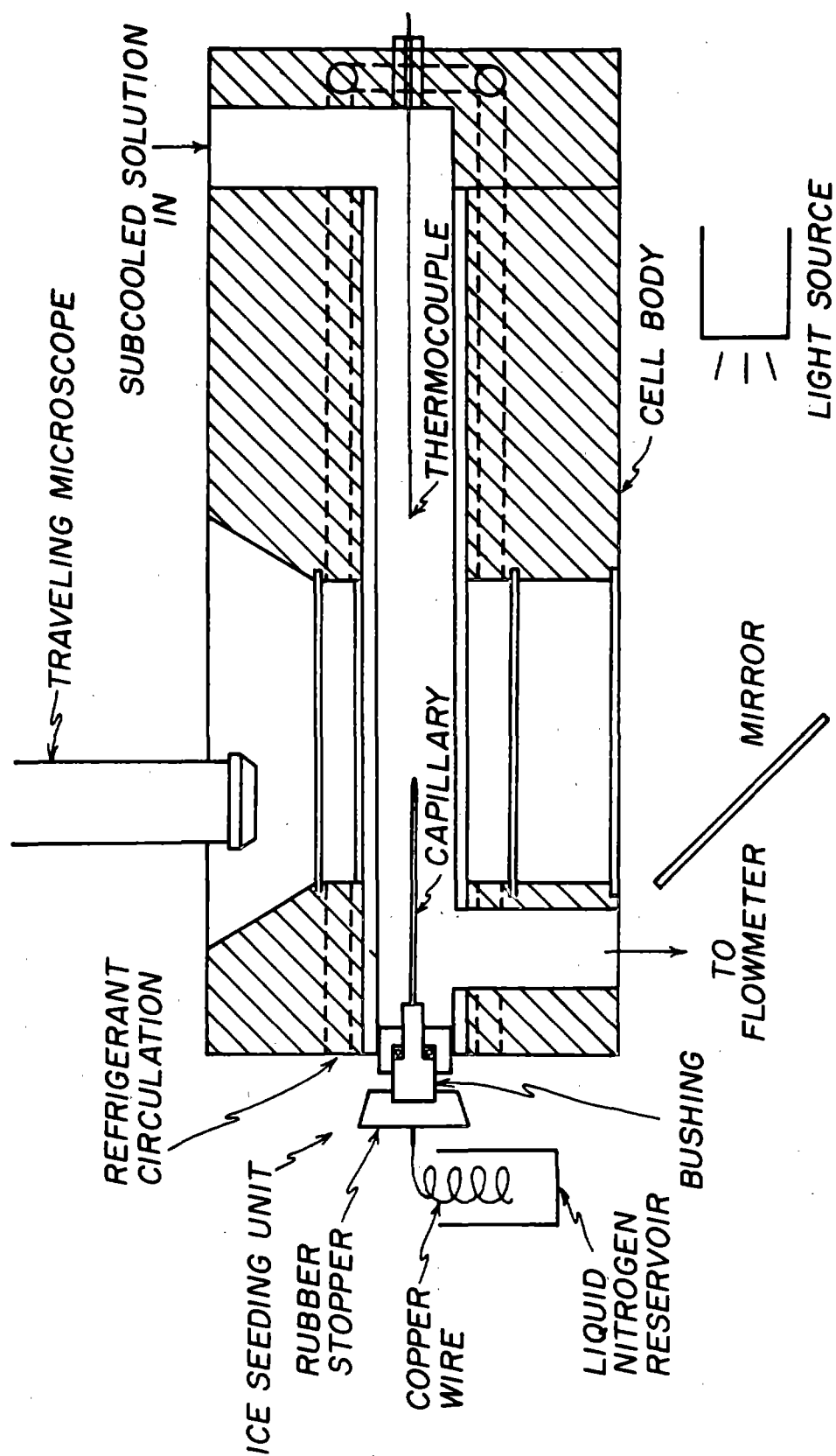


FIGURE 5B : ICE CRYSTAL GROWTH APPARATUS - DETAIL OF CRYSTAL GROWTH CELL

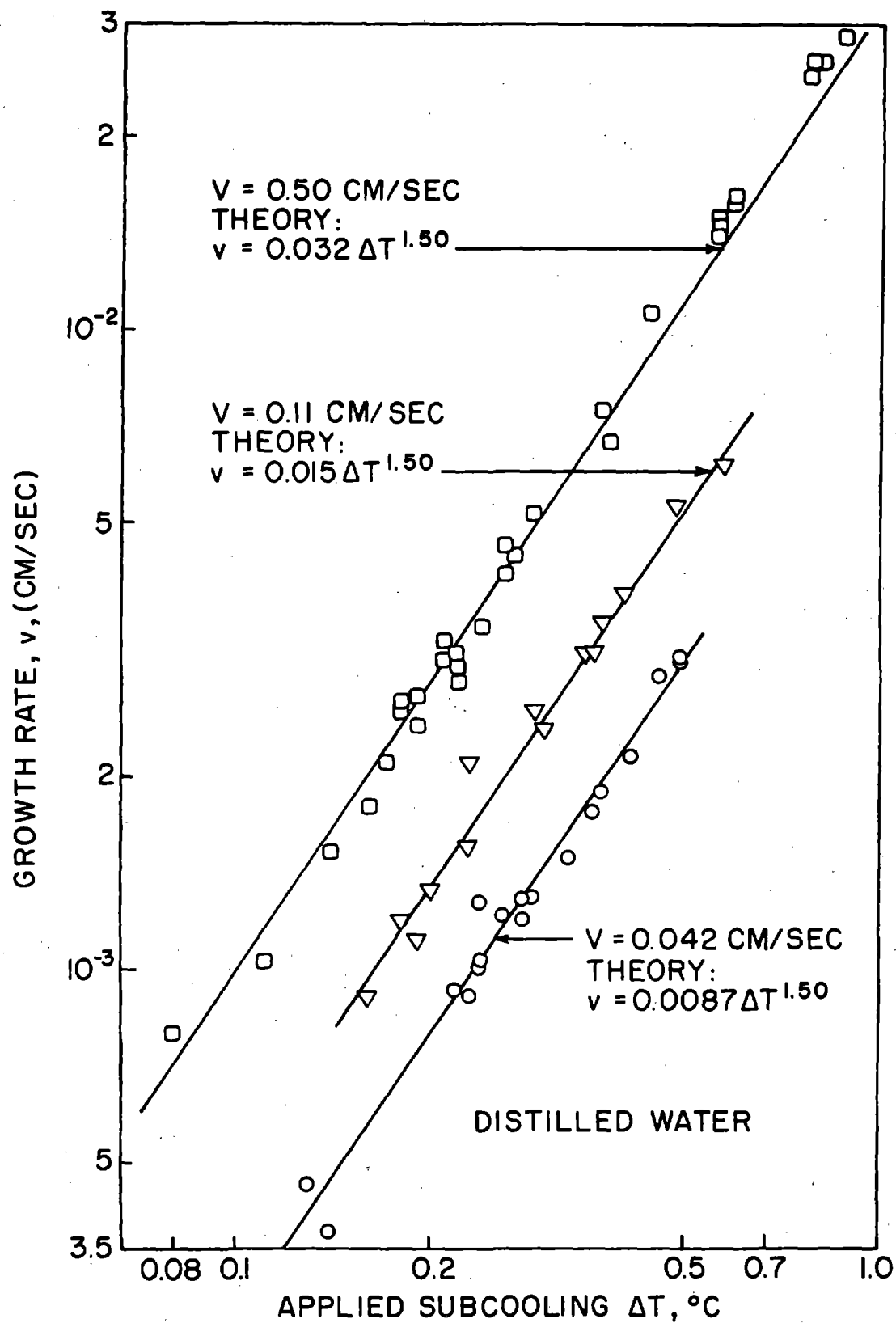


FIGURE 6 : ICE CRYSTAL GROWTH RATE VS. SUBCOOLING

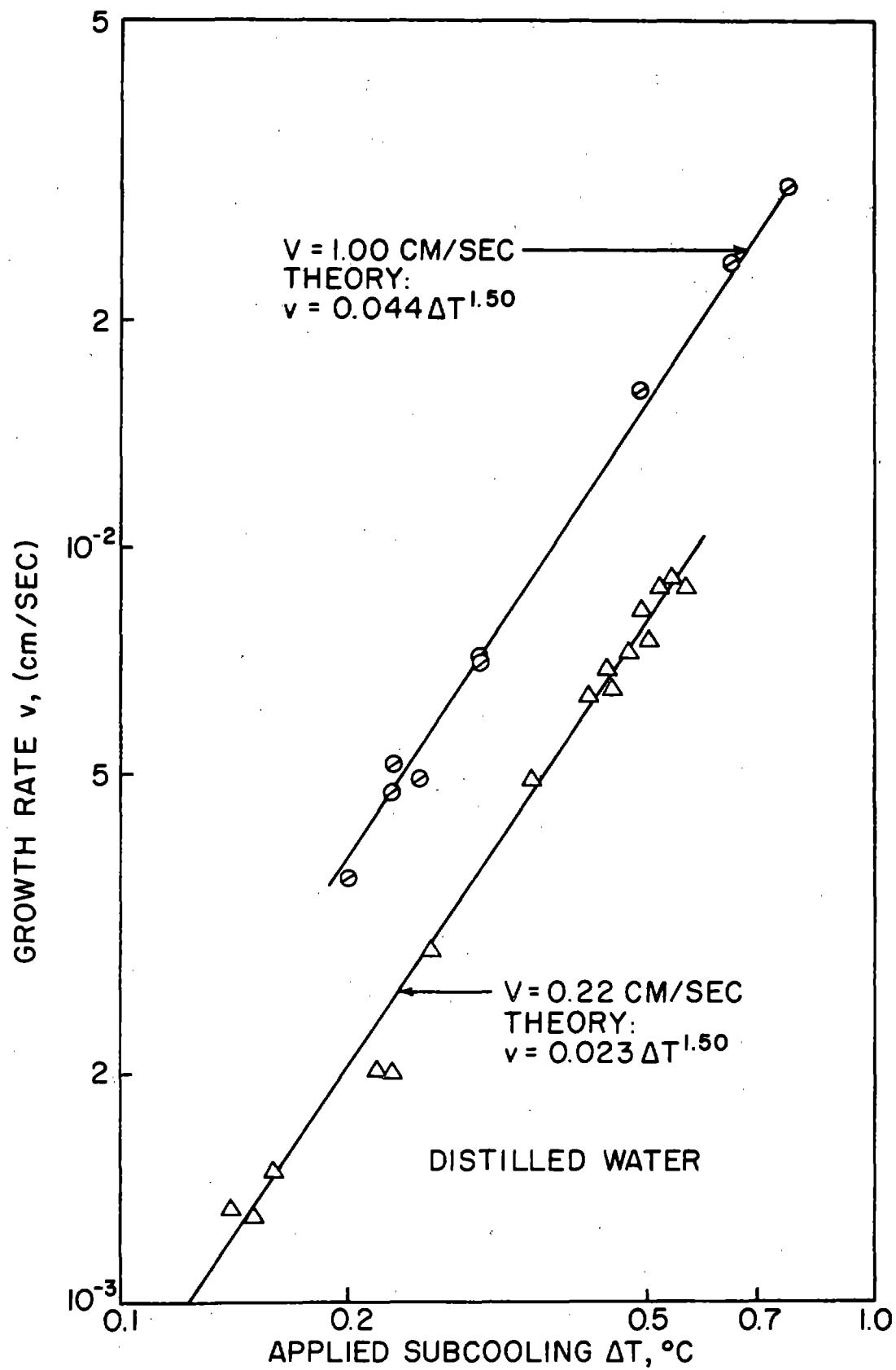


FIGURE 7 : ICE CRYSTAL GROWTH RATE VS. SUBCOOLING

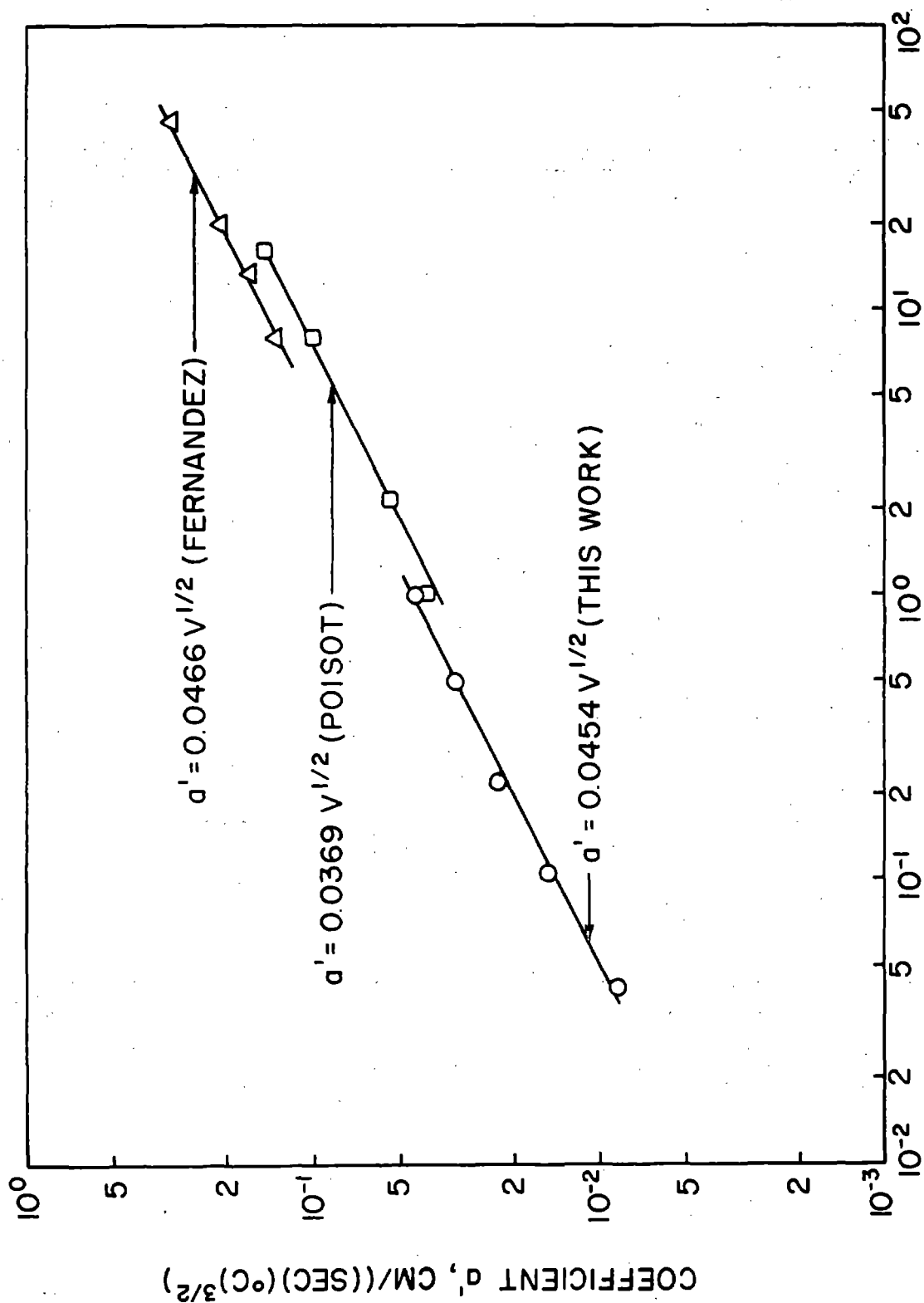


FIGURE 8 : COEFFICIENT α' VS. WATER VELOCITY IN $v = \alpha' \Delta T^{3/2}$

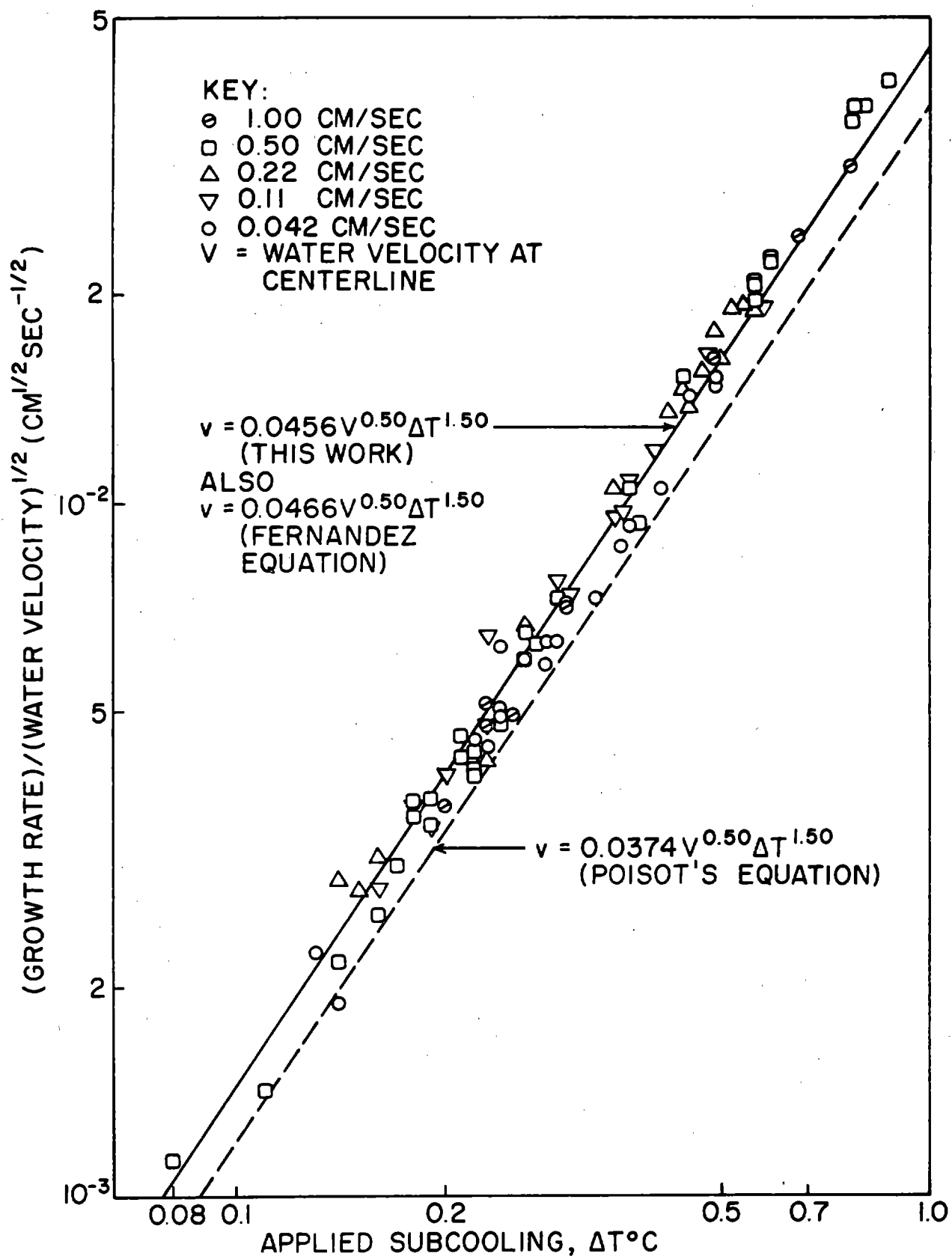


FIGURE 9 : ICE CRYSTAL GROWTH RATE DATA IN SUBCOOLED DISTILLED WATER

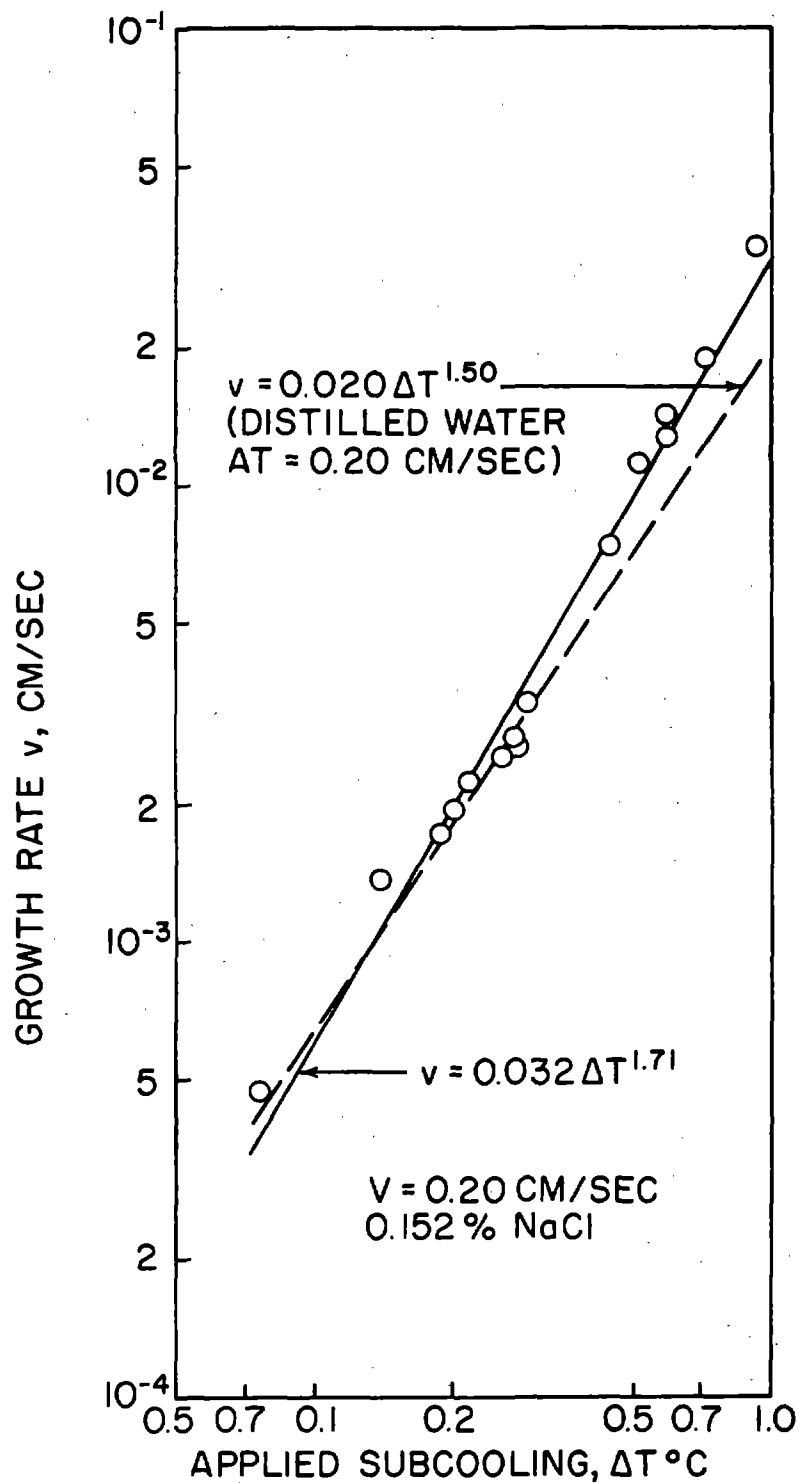


FIGURE 10 : ICE CRYSTAL GROWTH RATE VS.
 SUBCOOLING IN 0.152 % NaCl
 SOLUTION: $V = 0.20$ CM/SEC

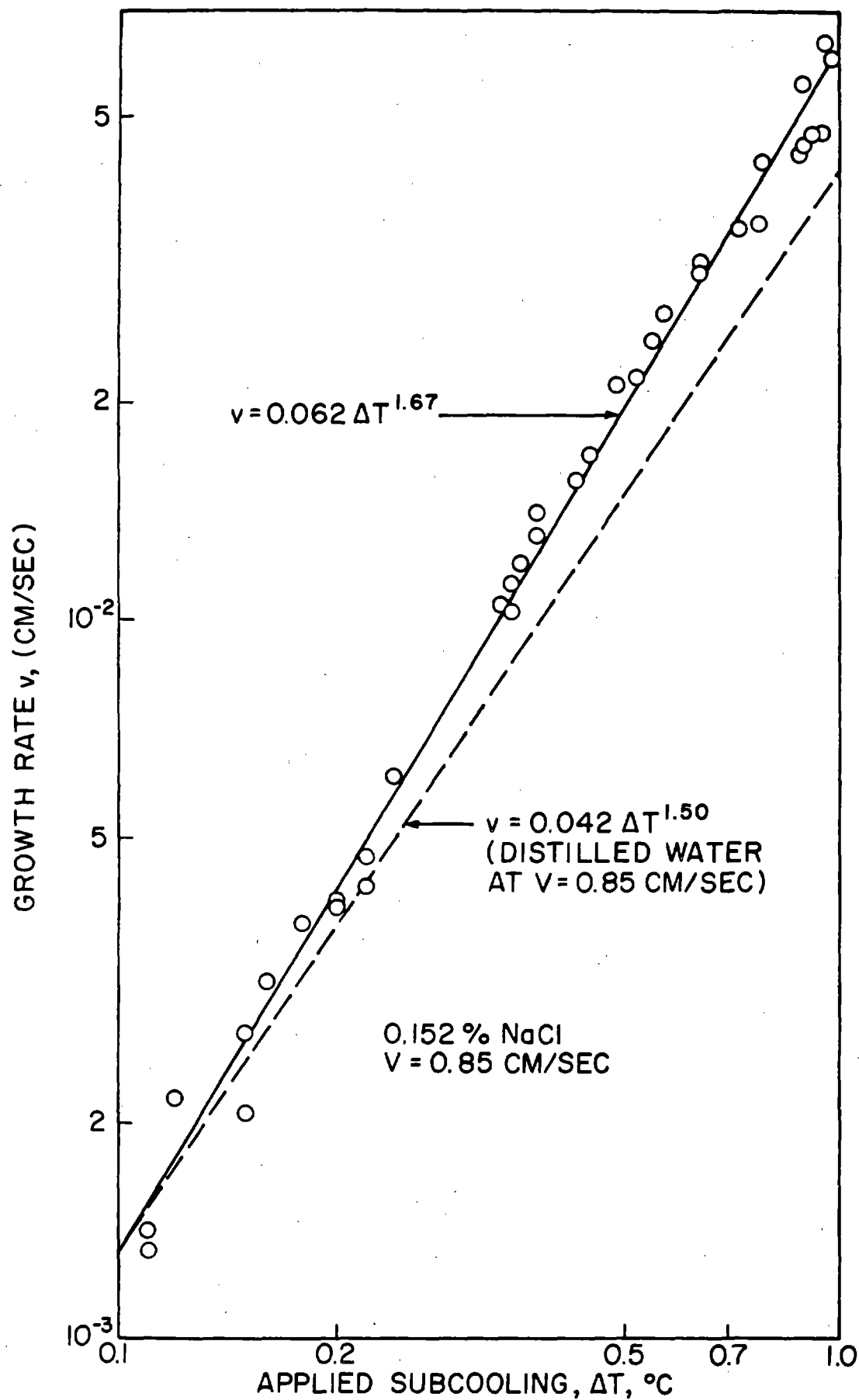


FIGURE II : ICE CRYSTAL GROWTH RATE VS.
SUBCOOLING IN 0.152 % NaCl SOLUTION:
 $V = 0.85$ CM/SEC

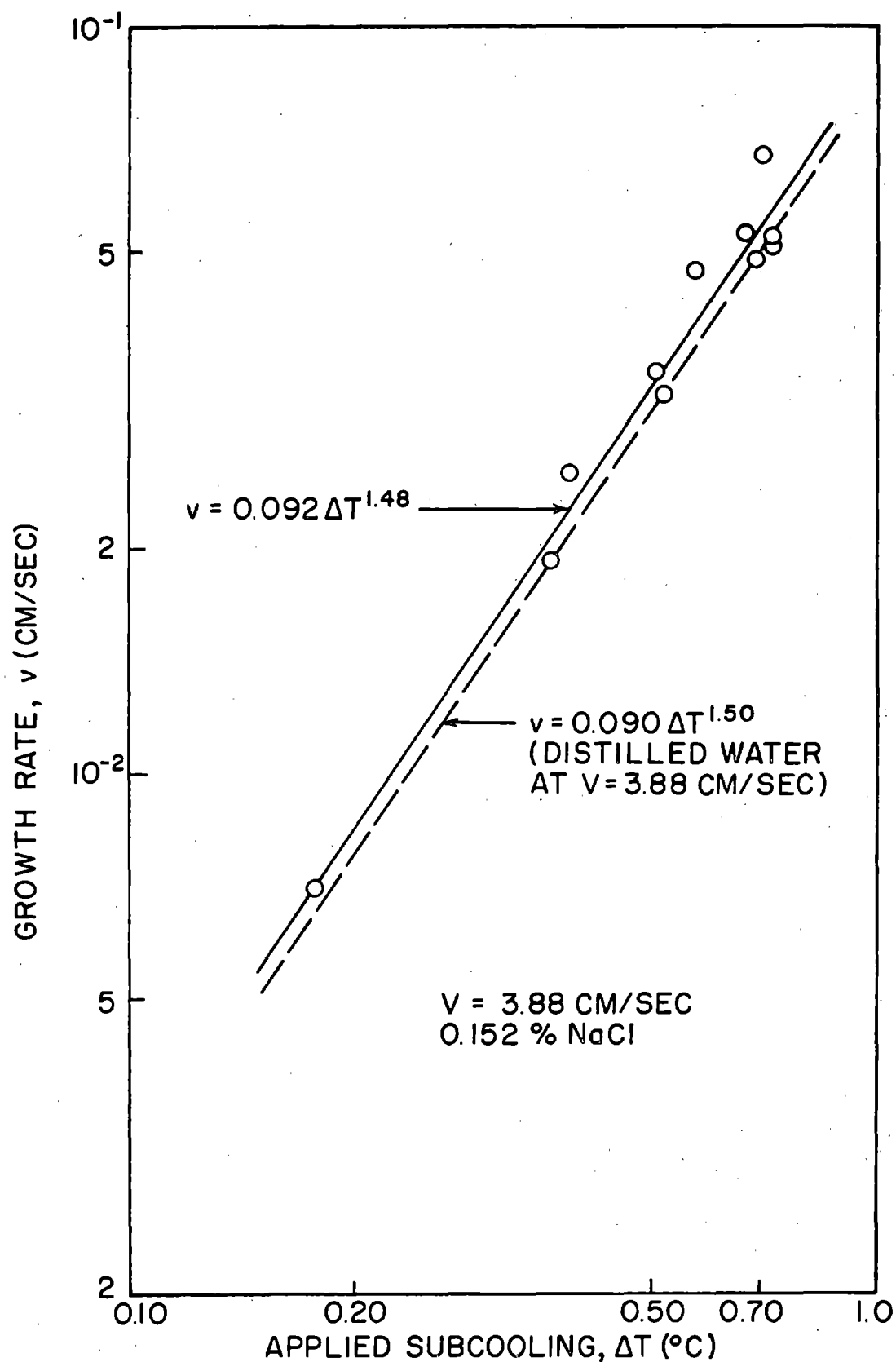


FIGURE 12 : ICE CRYSTAL GROWTH RATE VS. SUBCOOLING IN 0.152 % NaCl SOLUTION: $V = 3.88$ CM/SEC

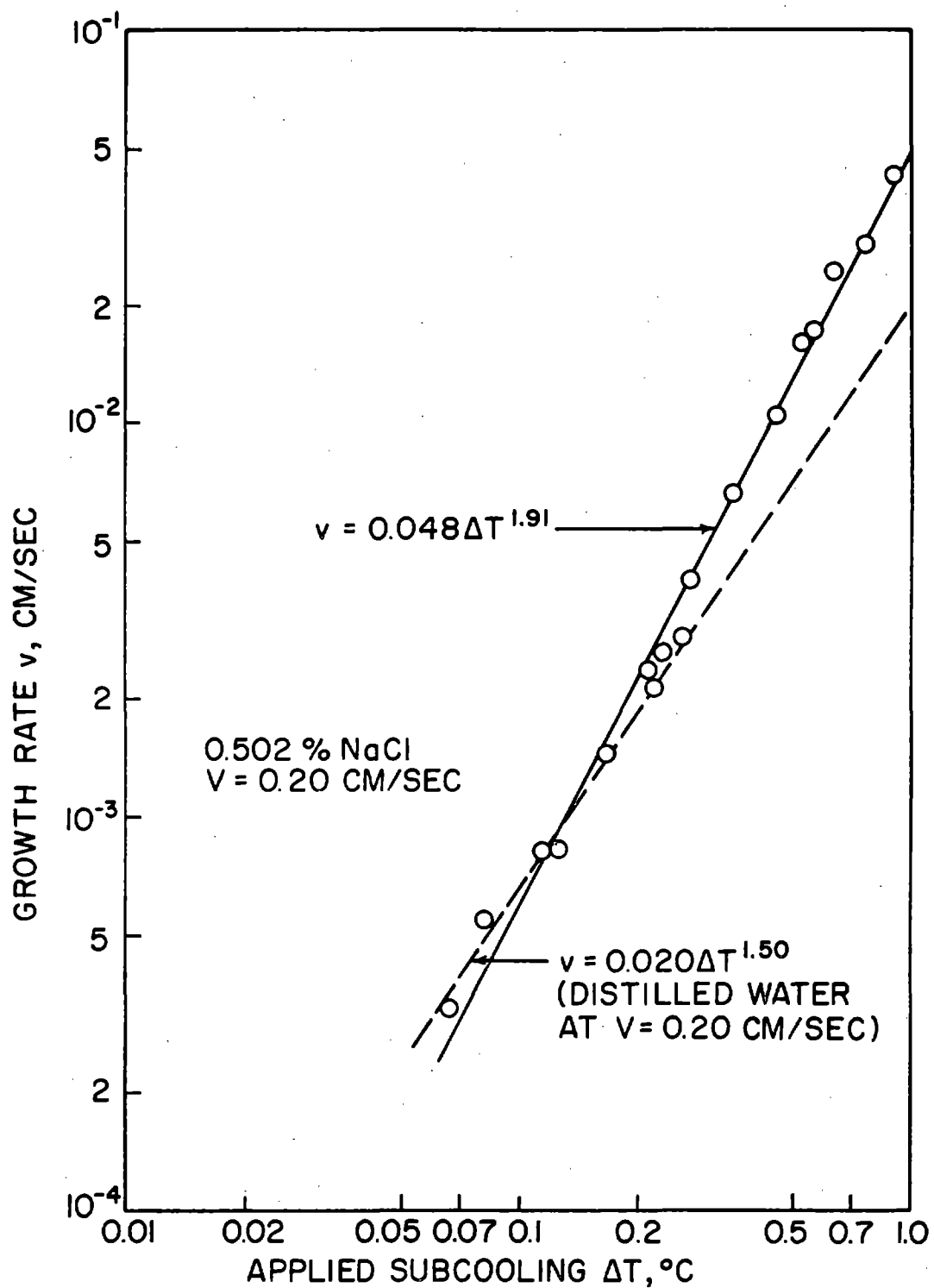


FIGURE 13 : ICE CRYSTAL GROWTH RATE VS.
SUBCOOLING IN 0.502 % NaCl SOLUTION:
V = 0.20 CM/SEC

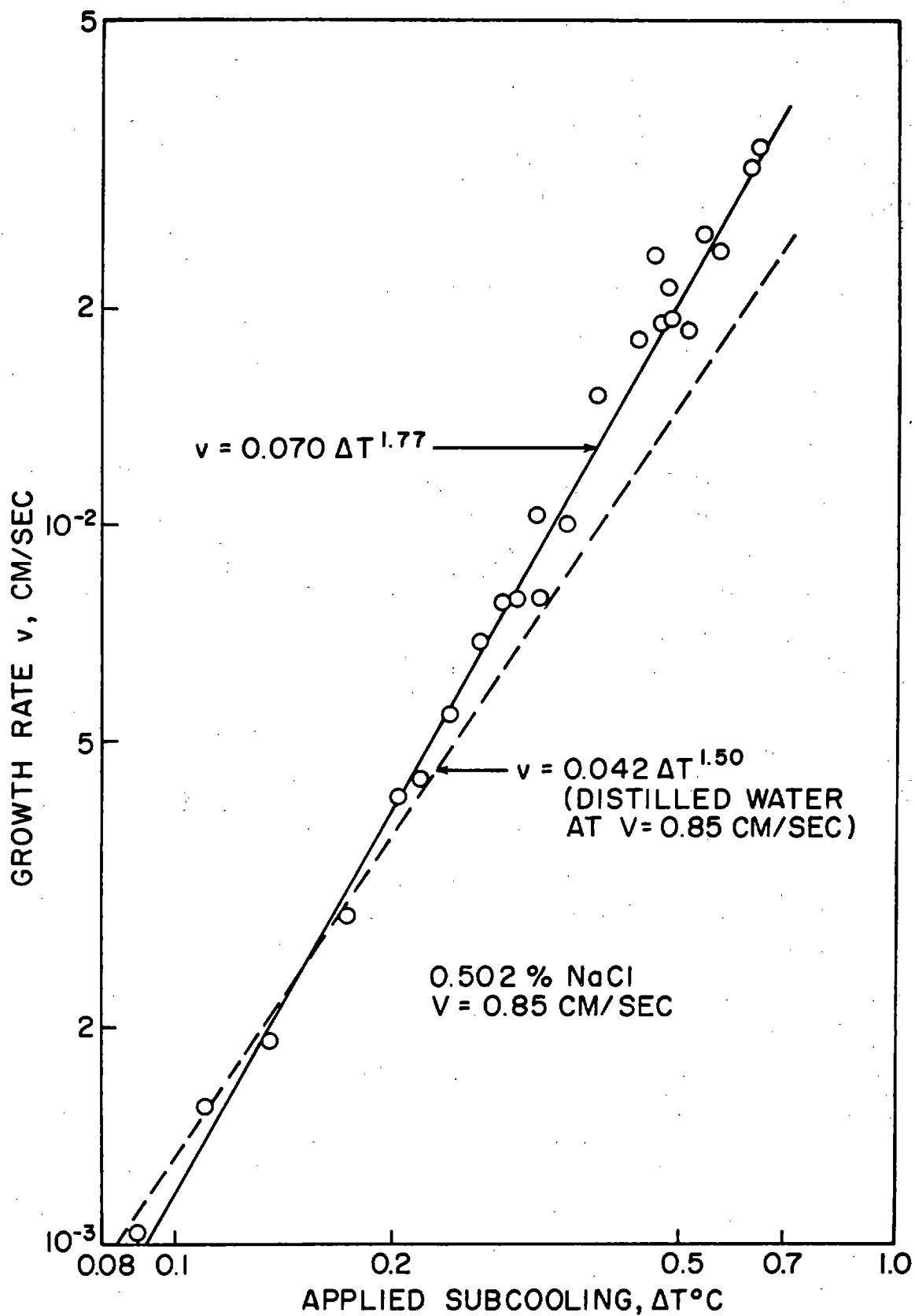


FIGURE 14 : ICE CRYSTAL GROWTH RATE VS.
 SUBCOOLING IN 0.502 % NaCl SOLUTION:
 $v = 0.85$ CM/SEC

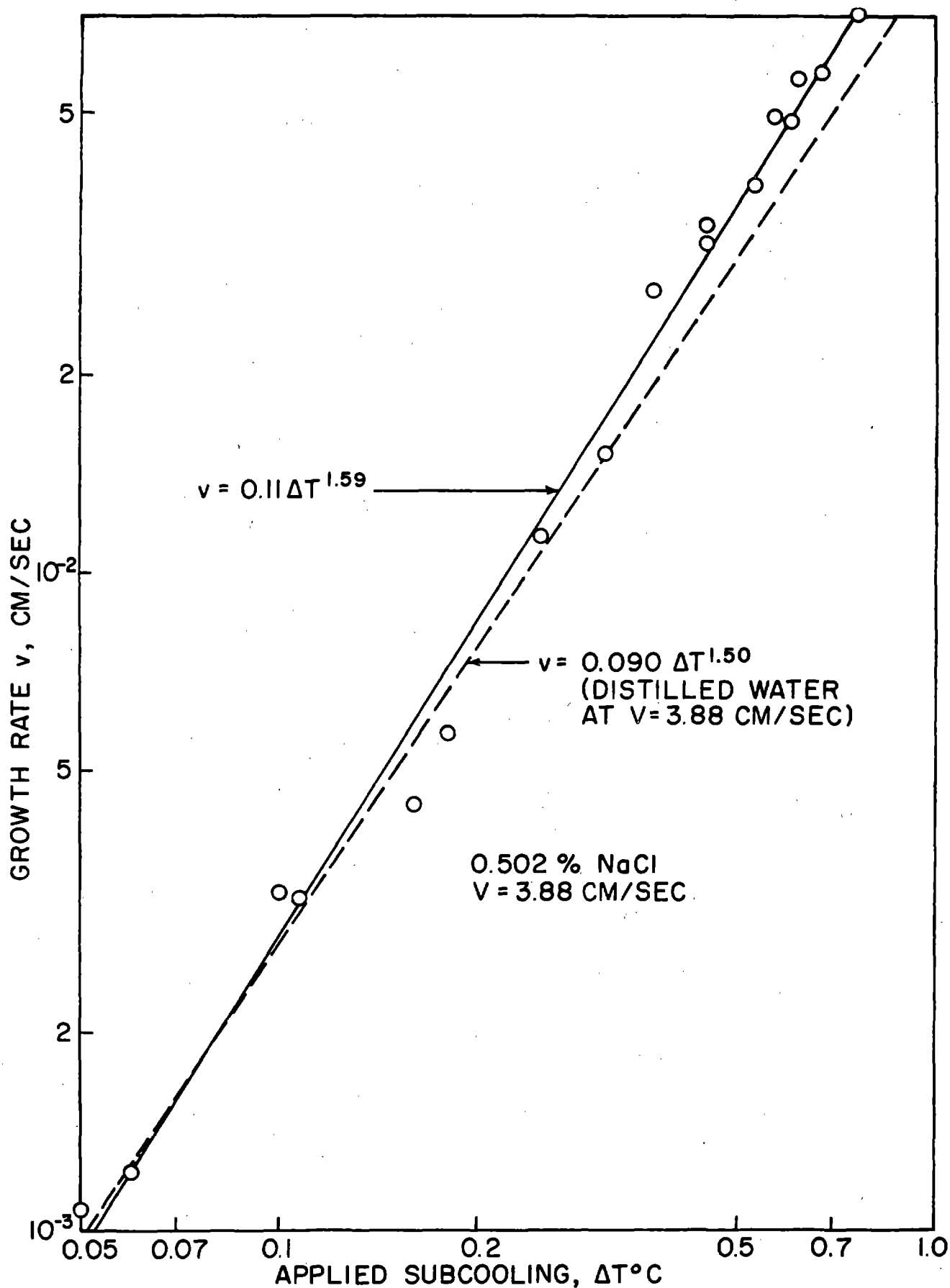


FIGURE 15 : ICE CRYSTAL GROWTH RATE VS. SUBCOOLING IN
 0.502 % NaCl SOLUTION: $V = 3.88$ CM/SEC

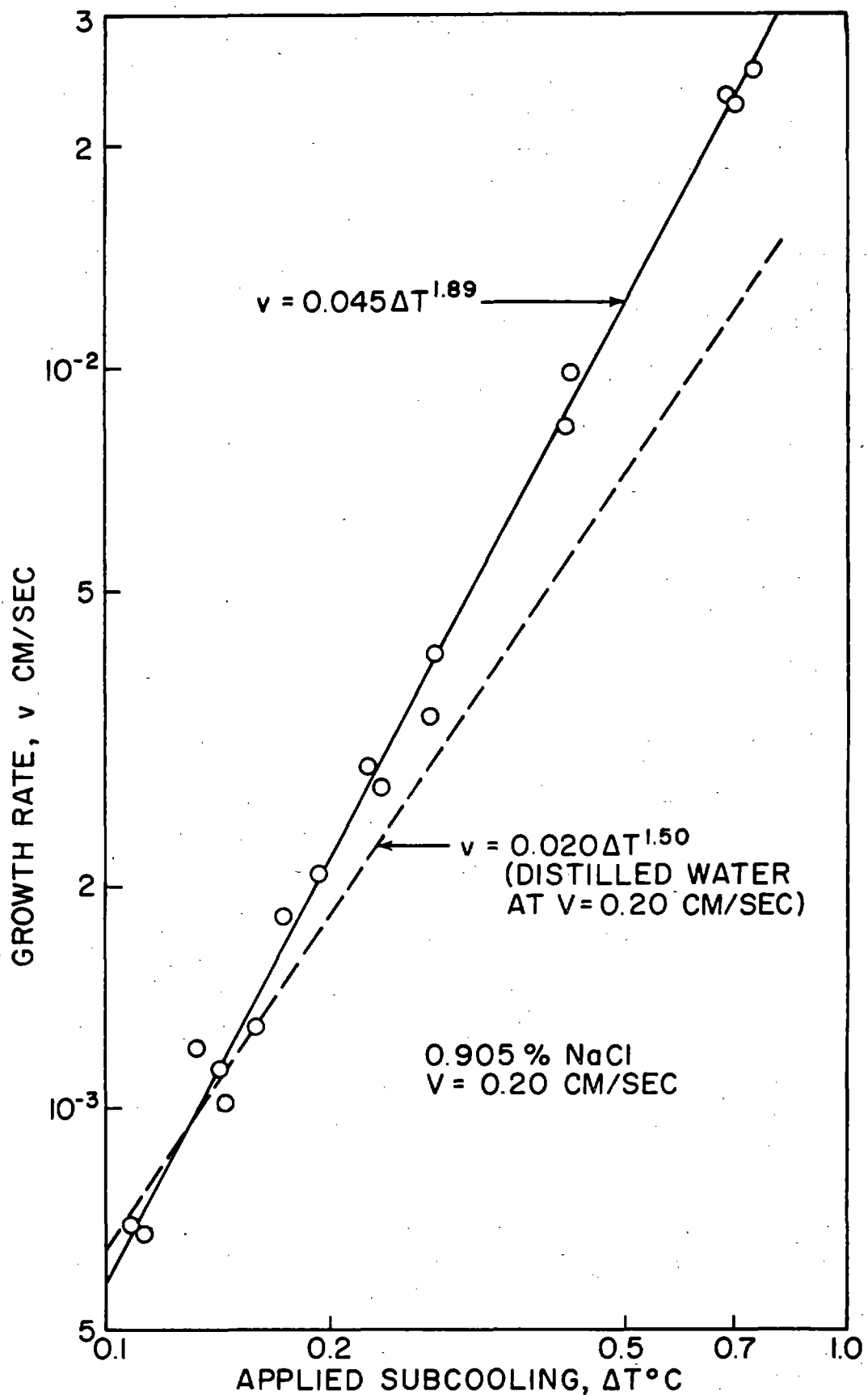


FIGURE 16 : ICE CRYSTAL GROWTH RATE VS.
 SUBCOOLING IN 0.905 % NaCl SOLUTION:
 $v = 0.20$ CM/SEC

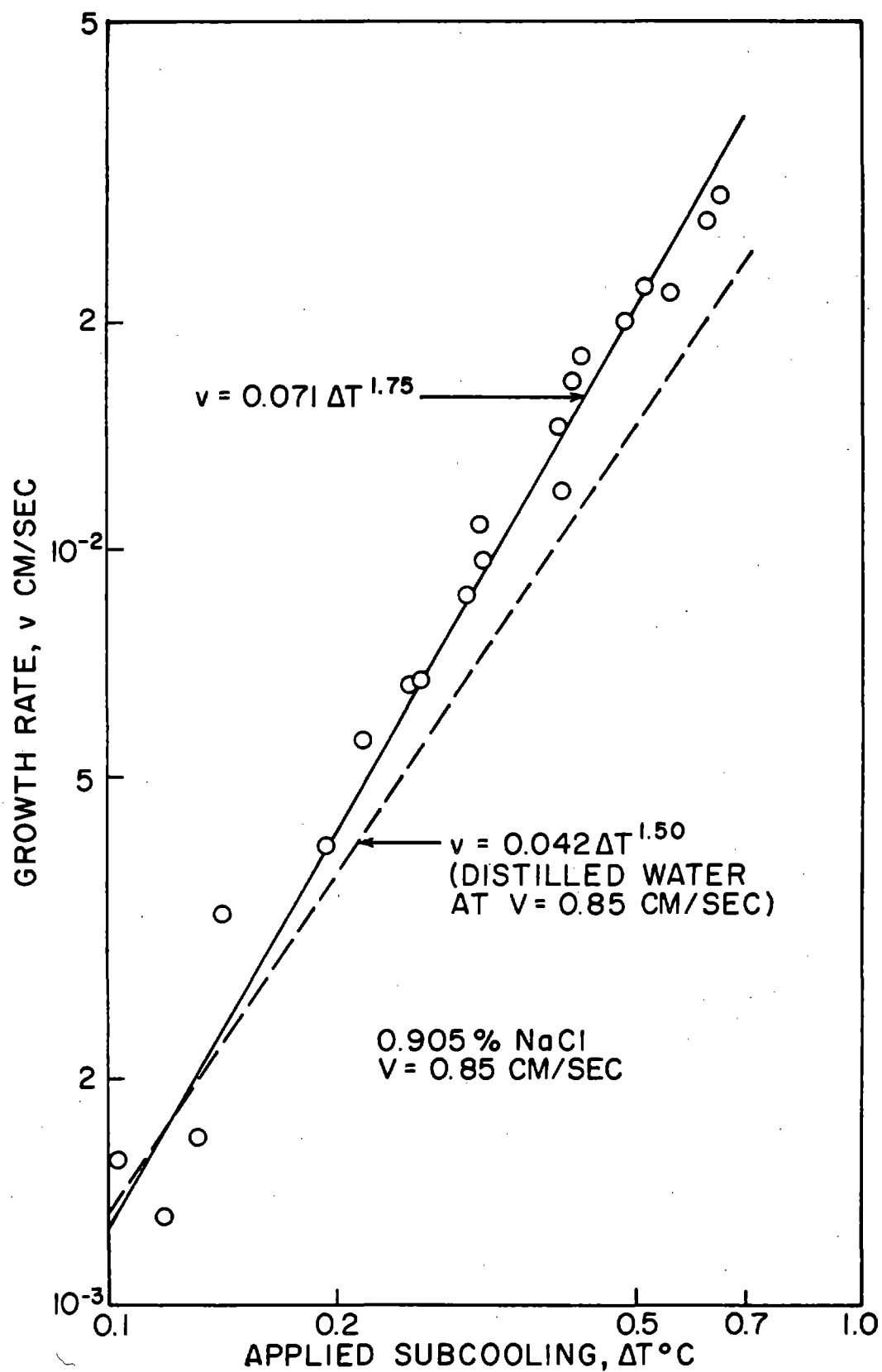


FIGURE 17 : ICE CRYSTAL GROWTH RATE VS. SUBCOOLING IN 0.905 % NaCl SOLUTION: $V = 0.85$ CM/ SEC

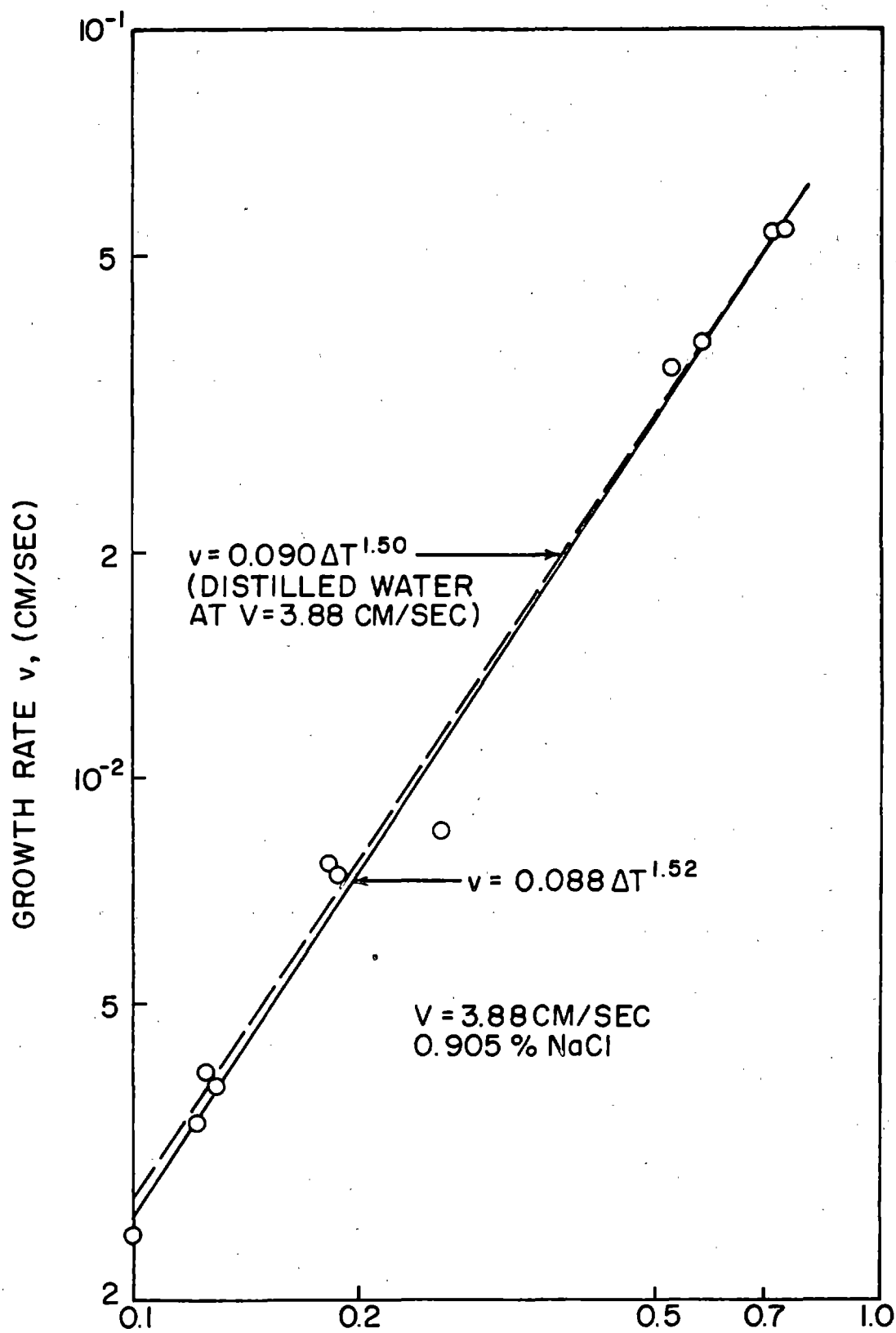


FIGURE 18 : ICE CRYSTAL GROWTH RATE VS.
 SUBCOOLING IN 0.905 % NaCl
 SOLUTION: $V = 3.88$ CM/SEC

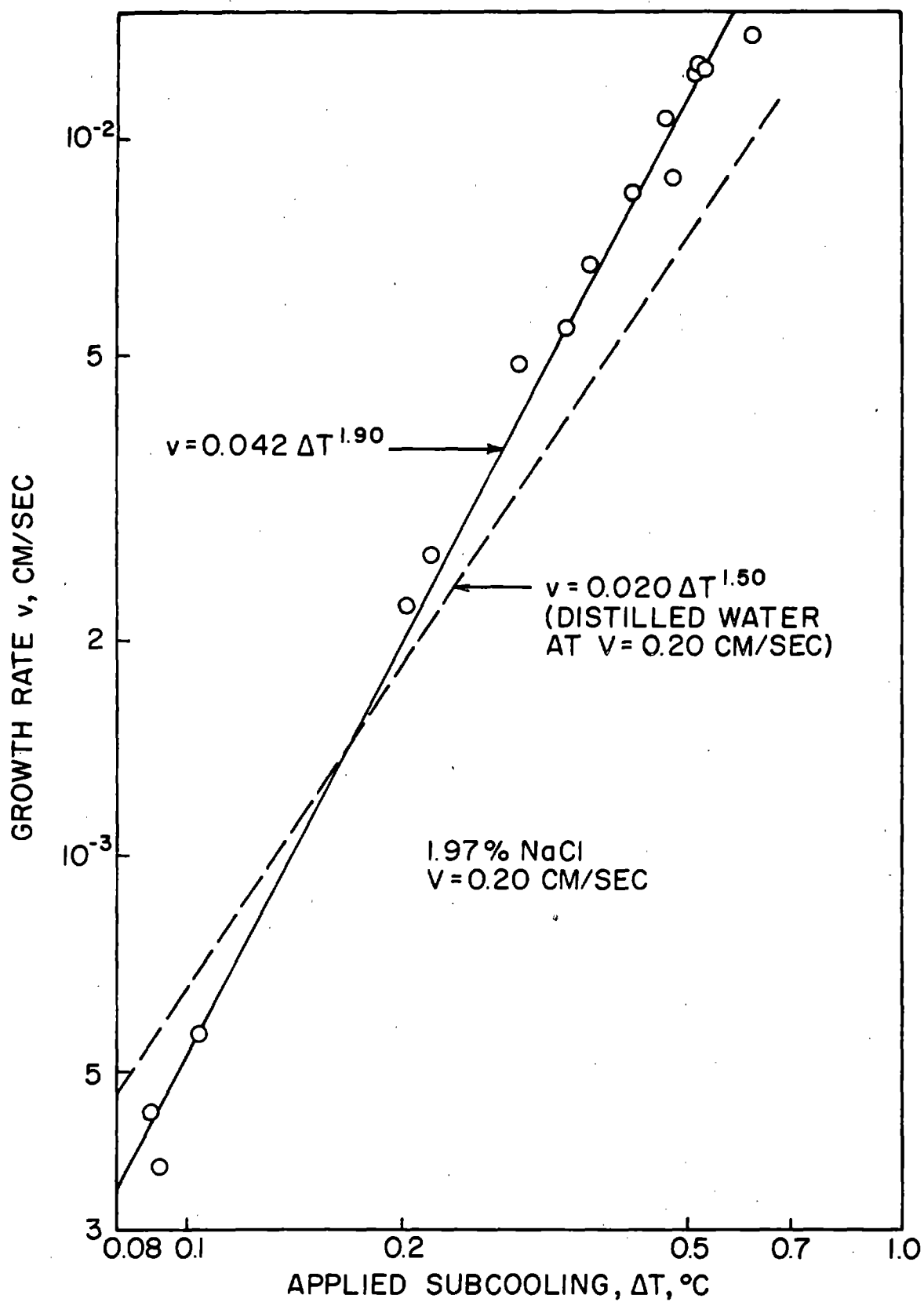


FIGURE 19 : ICE CRYSTAL GROWTH RATE VS.
 SUBCOOLING IN 1.97 % NaCl SOLUTION:
 $V = 0.20$ CM/SEC

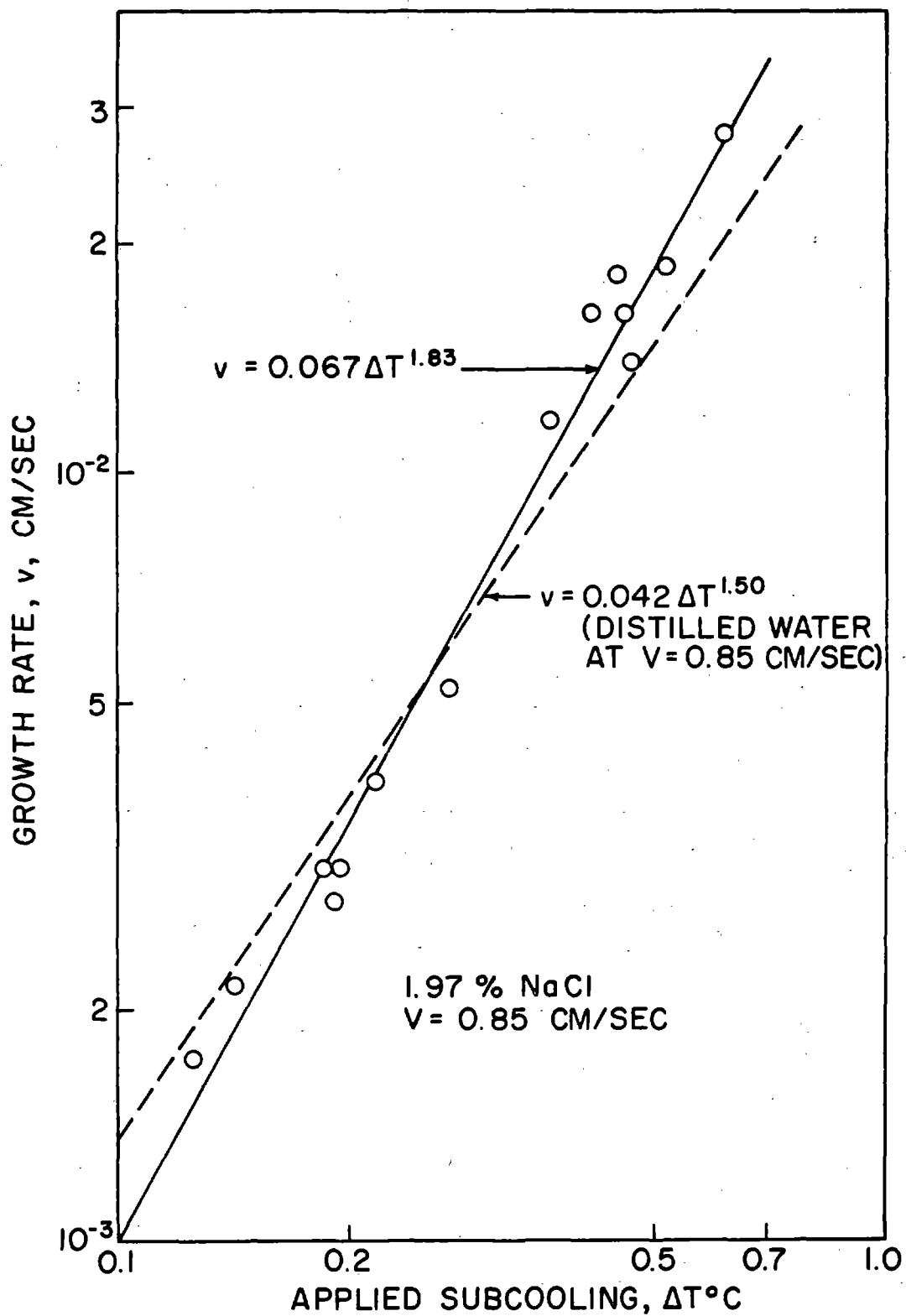


FIGURE 20 : ICE CRYSTAL GROWTH RATE VS.
 SUBCOOLING IN 1.97 % NaCl SOLUTION
 $V = 0.85$ CM/SEC

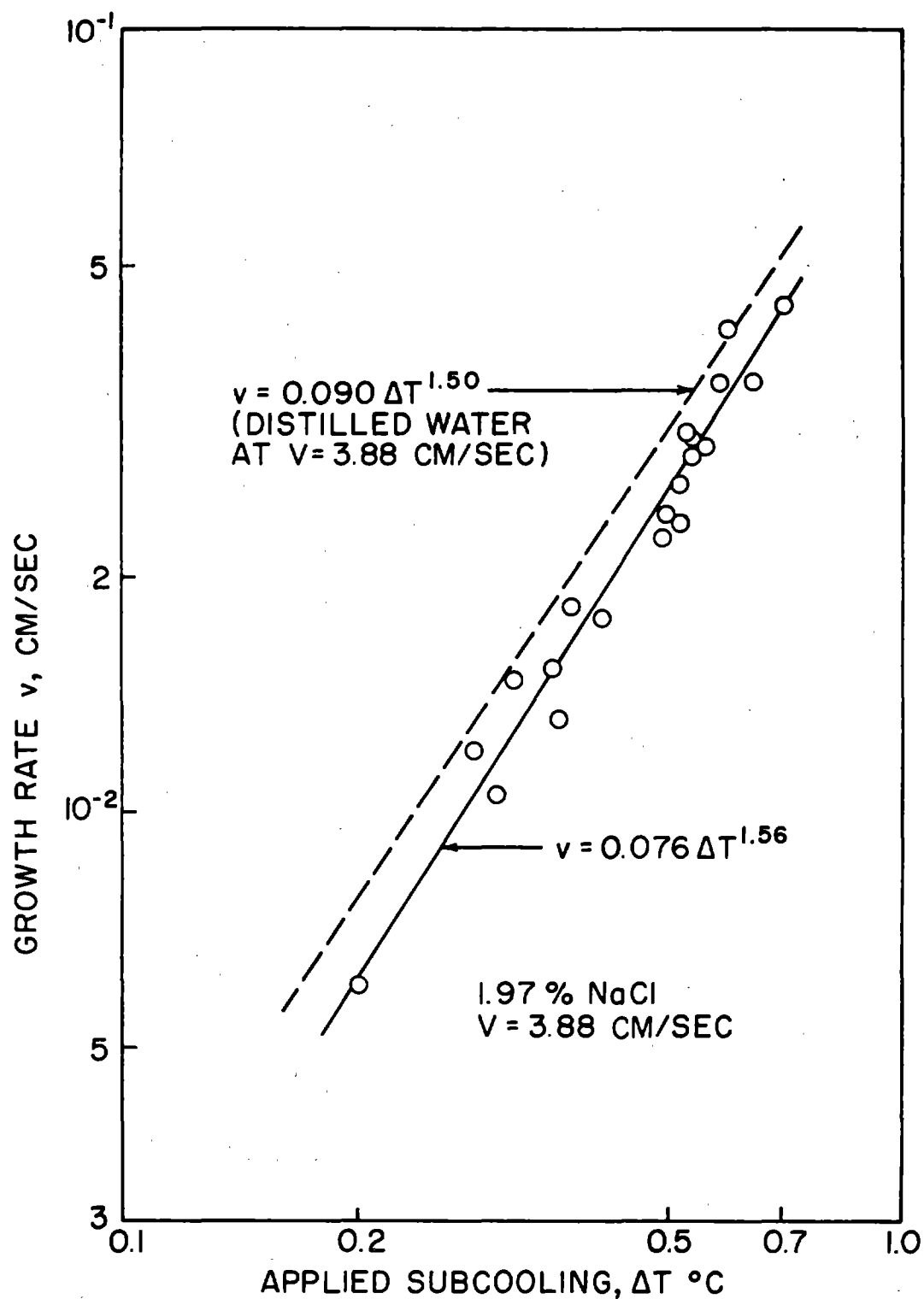


FIGURE 21 : ICE CRYSTAL GROWTH RATE VS.
 SUBCOOLING IN 1.97 % NaCl SOLUTION:
 $V = 3.88$ CM/SEC

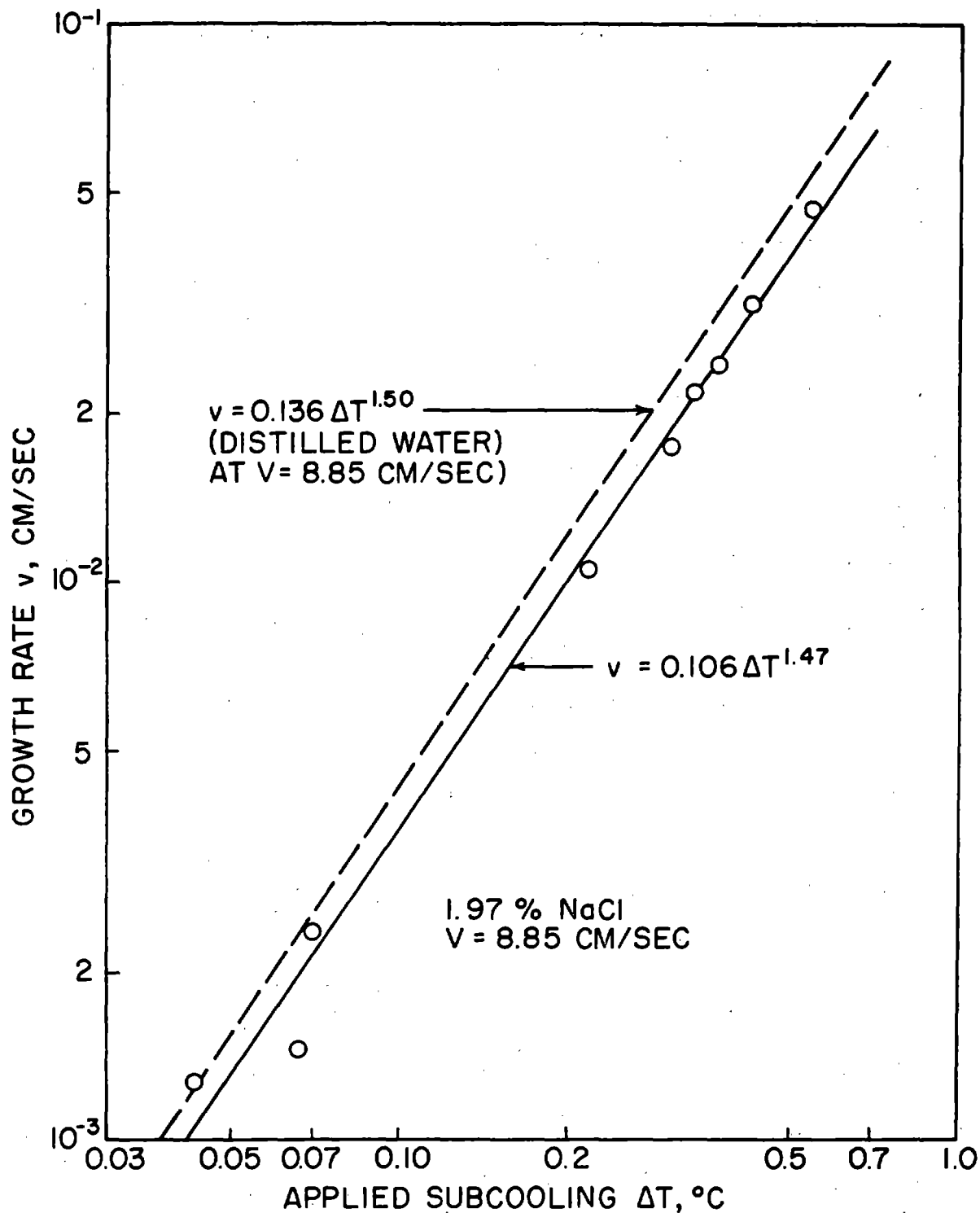


FIGURE 22 : ICE CRYSTAL GROWTH RATE VS.
 SUBCOOLING IN 1.97 % NaCl SOLUTION:
 $V = 8.85$ CM/SEC

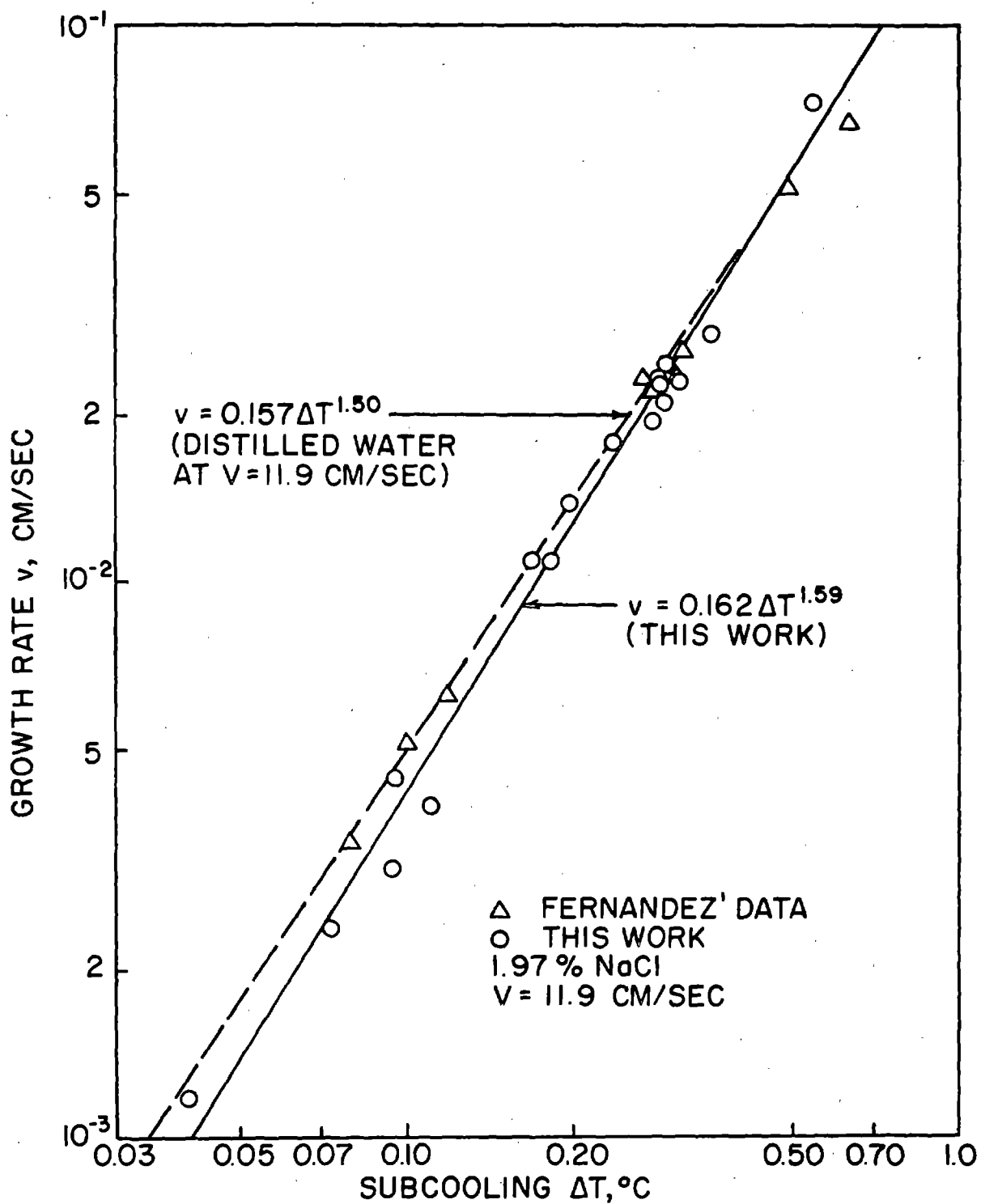


FIGURE 23 : ICE CRYSTAL GROWTH RATE VS. SUBCOOLING
IN 1.97 % NaCl SOLUTION: $V = 11.9$ CM/SEC

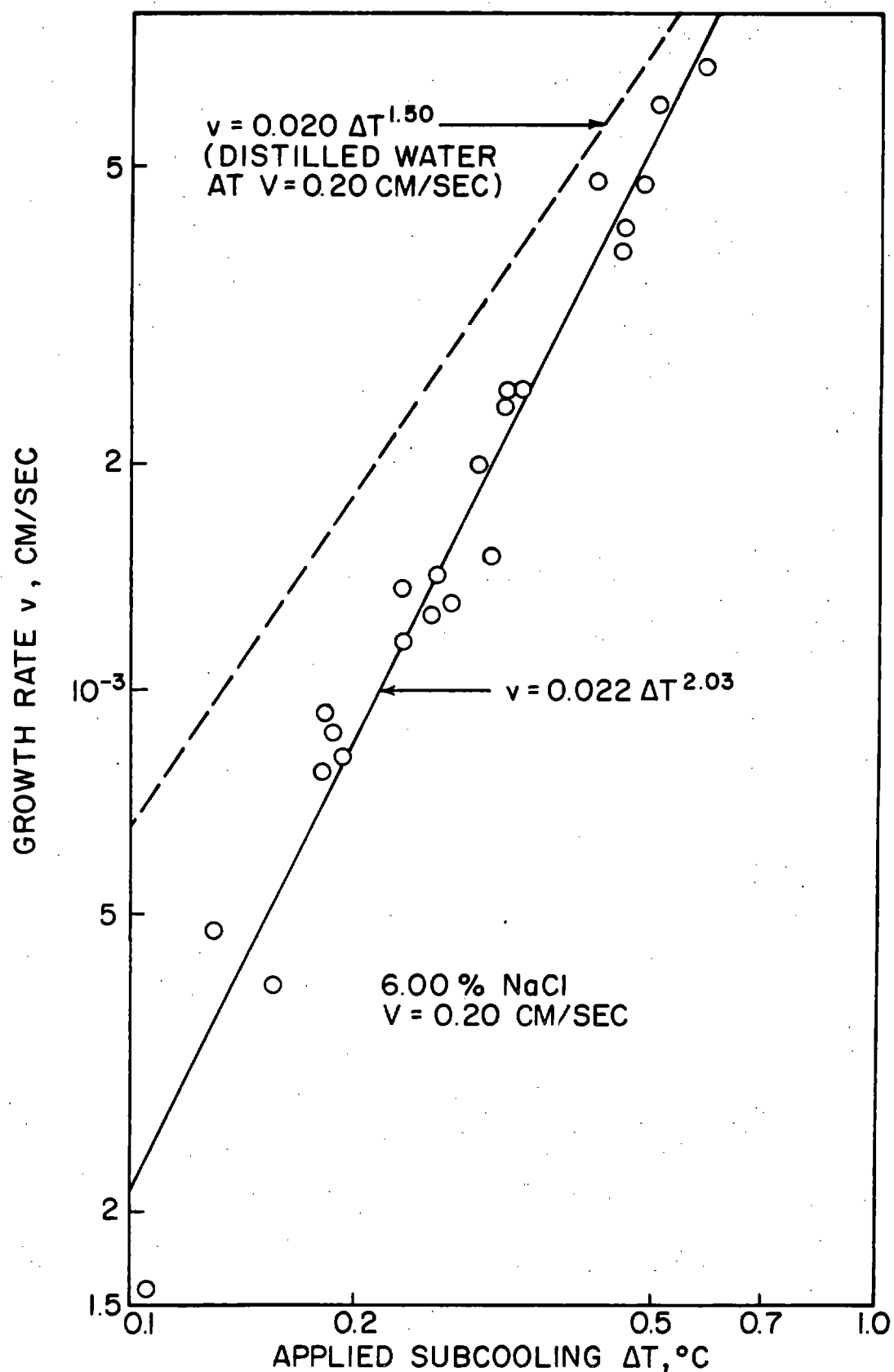


FIGURE 24 : ICE CRYSTAL GROWTH RATE VS.
 SUBCOOLING IN 6.00 % NaCl SOLUTION:
 $V = 0.20$ CM/SEC

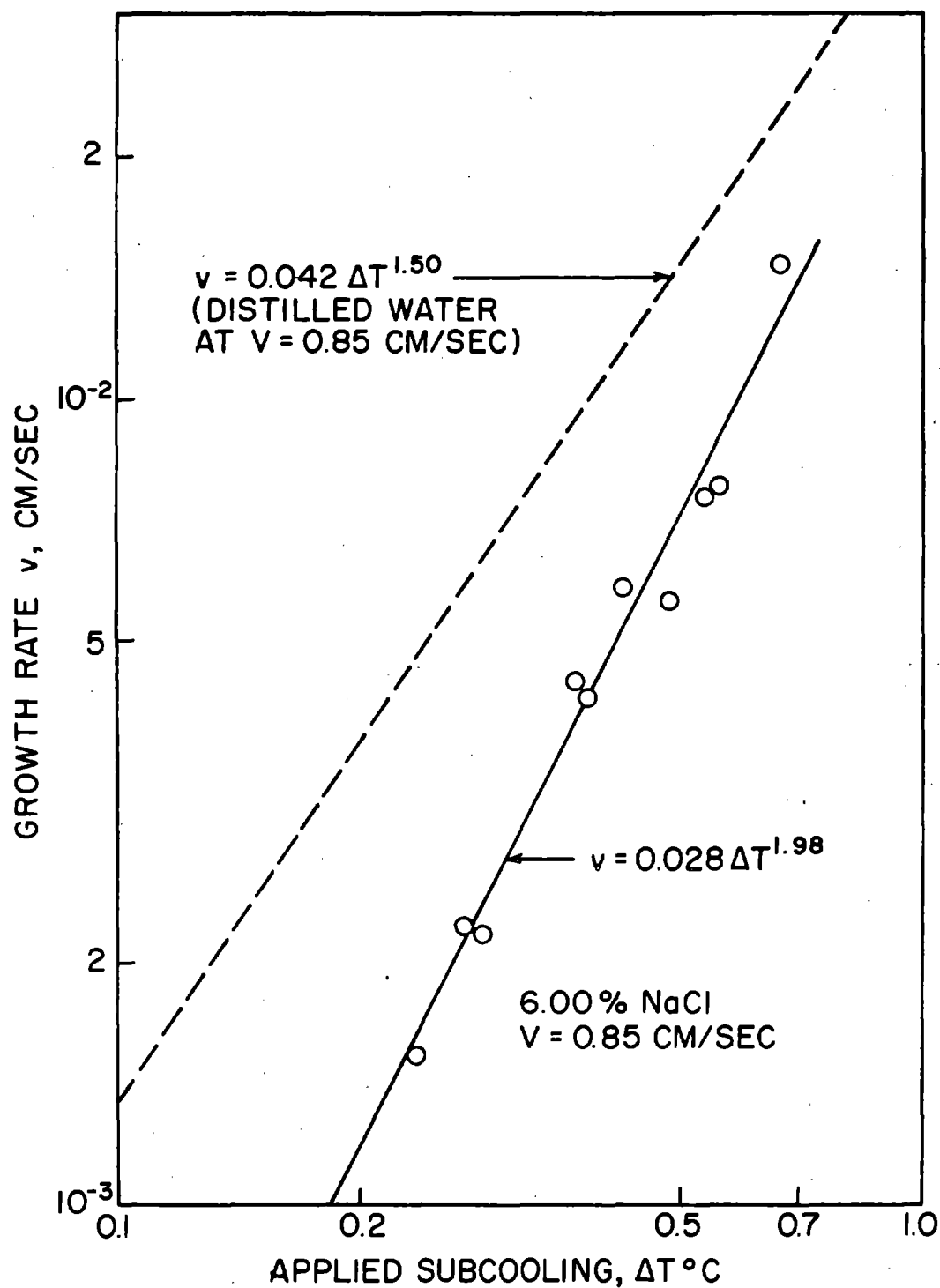


FIGURE 25 : ICE CRYSTAL GROWTH RATE VS.
 SUBCOOLING IN 6.00 % NaCl SOLUTION:
 $V = 0.85$ CM/SEC

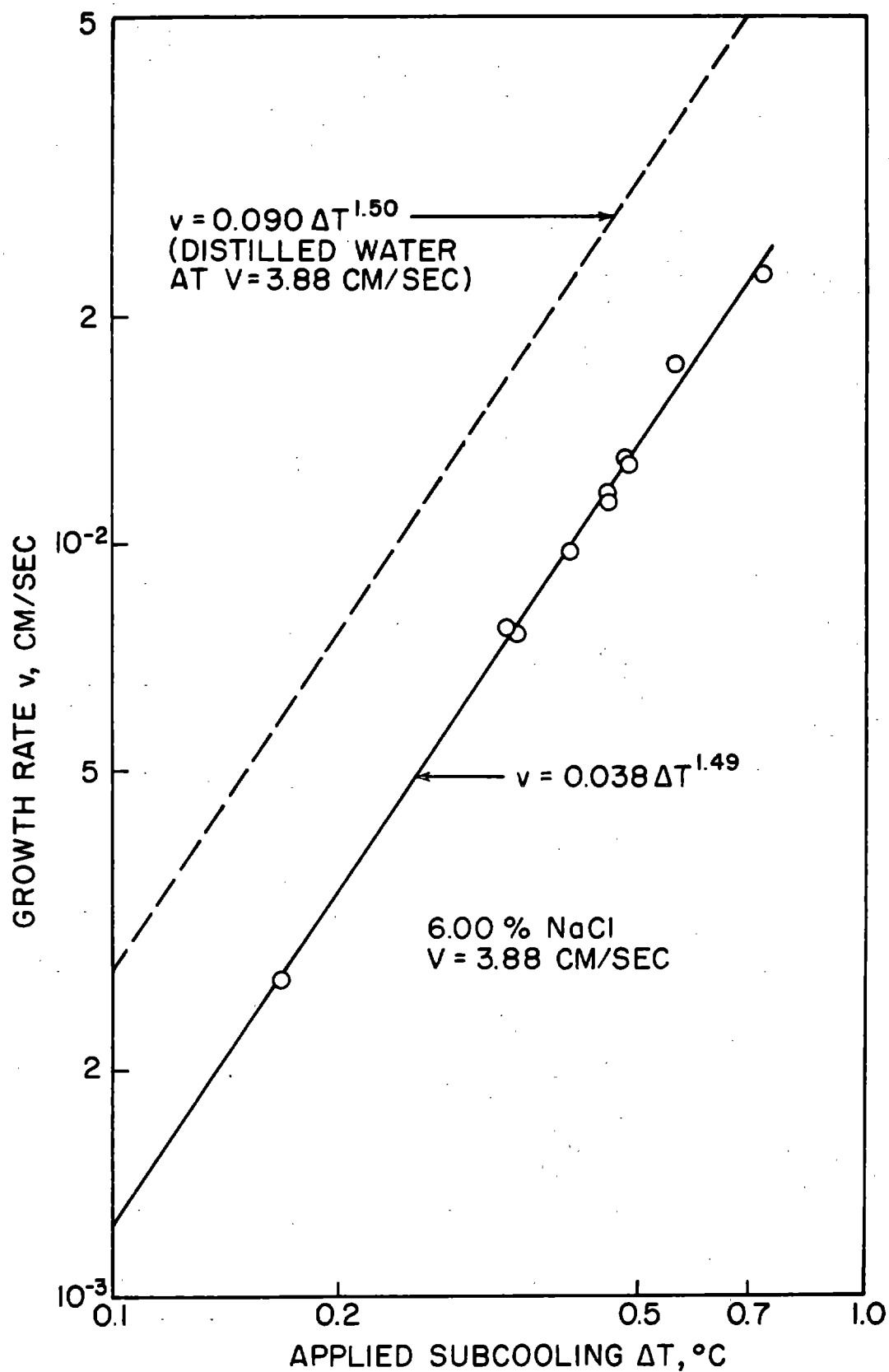


FIGURE 26 : ICE CRYSTAL GROWTH RATE VS.
 SUBCOOLING IN 6.00 % NaCl SOLUTION:
 $V = 3.88$ CM/ SEC

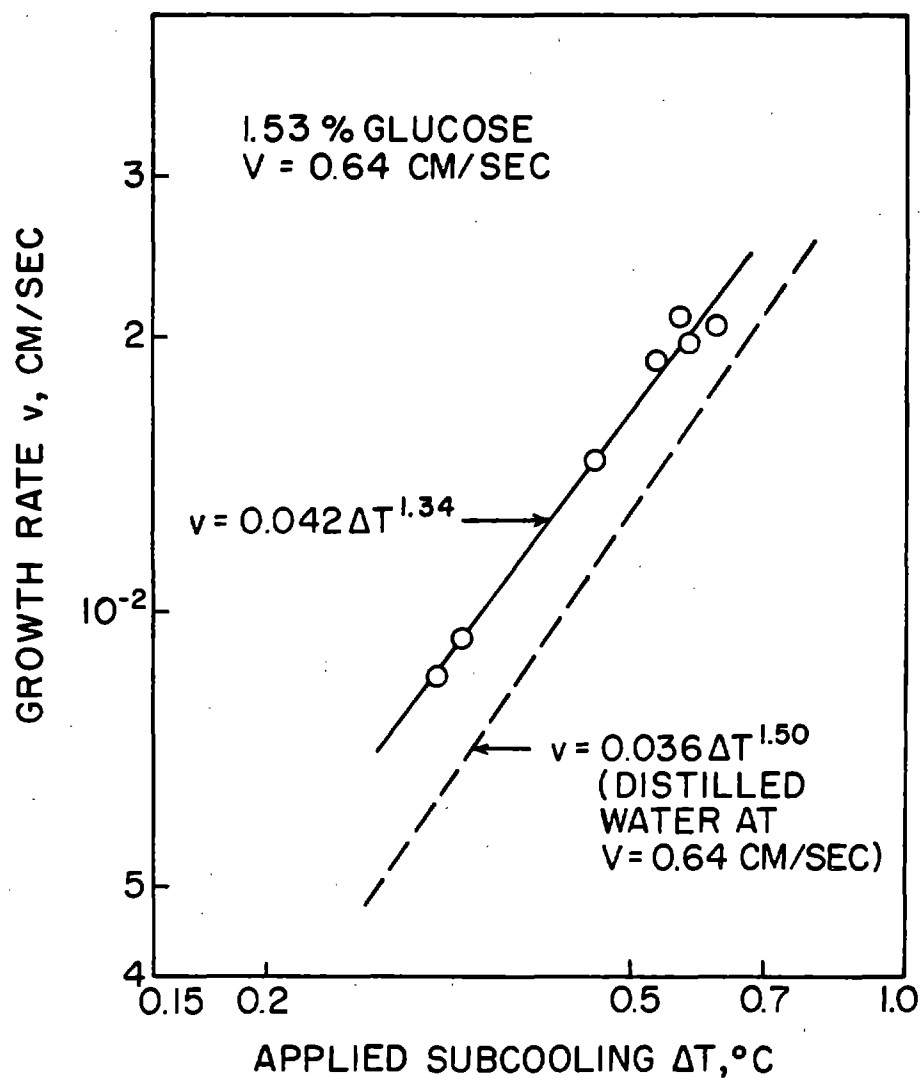


FIGURE 27 : ICE CRYSTAL GROWTH RATE VS.
SUBCOOLING IN 1.53 % GLUCOSE
SOLUTION: V = 0.64 CM/SEC

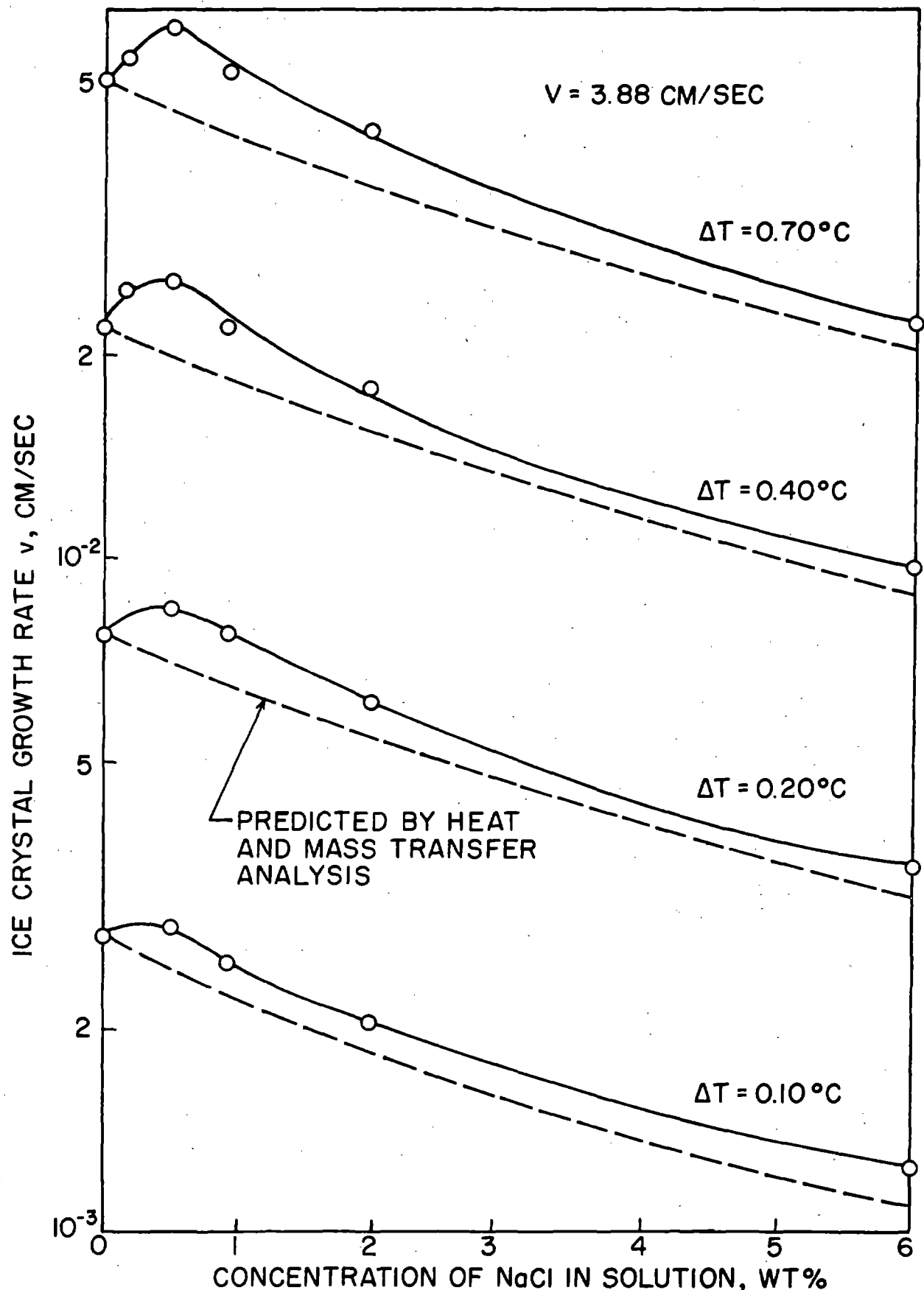


FIGURE 28 : ICE CRYSTAL GROWTH RATE VS. SOLUTION CONCENTRATION AS A FUNCTION OF SUBCOOLING: $V = 3.88$ CM/SEC

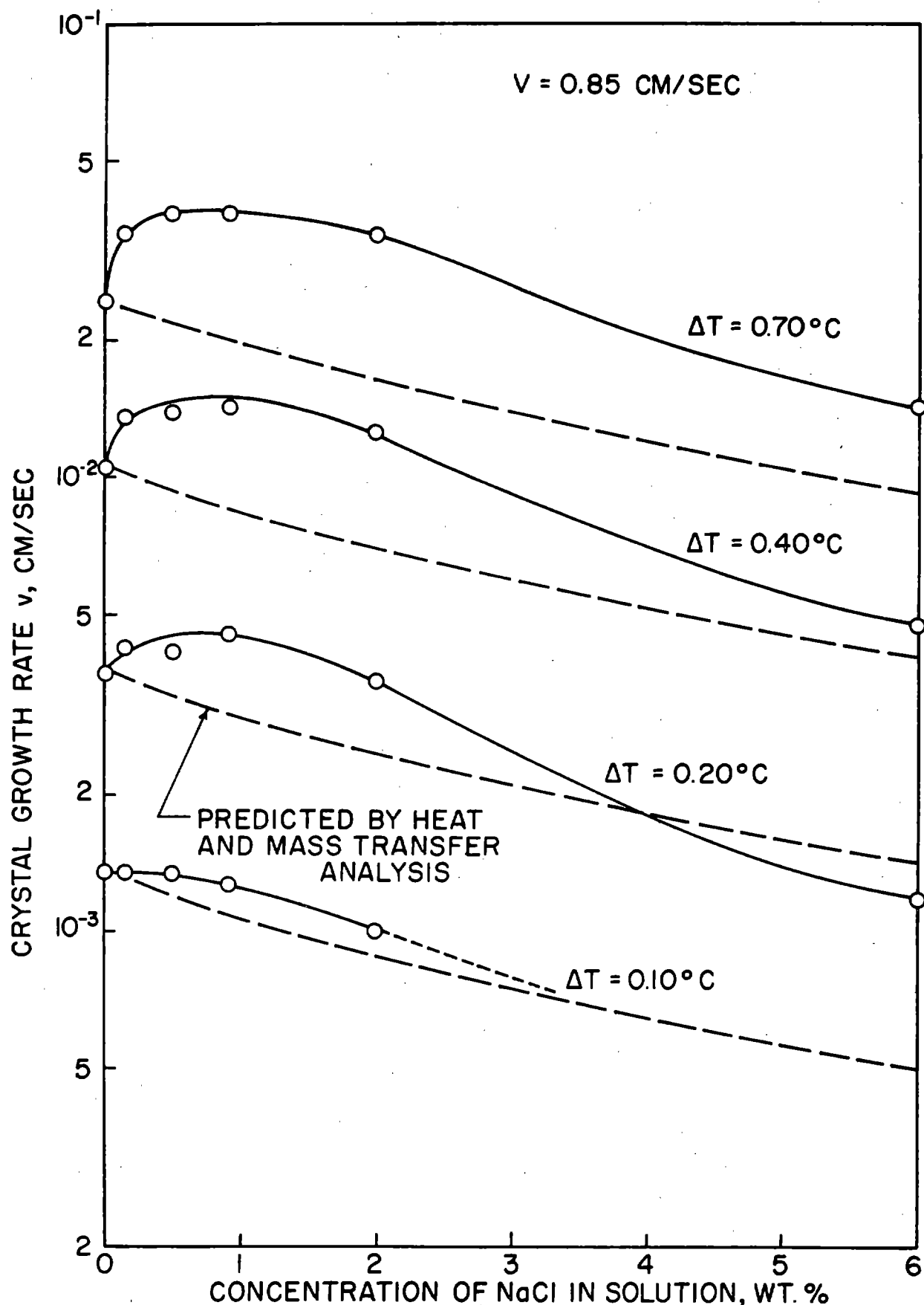


FIGURE 29 : ICE CRYSTAL GROWTH RATE VS. SOLUTION CONCENTRATION AS A FUNCTION OF SUBCOOLING: $V = 0.85$ CM/SEC

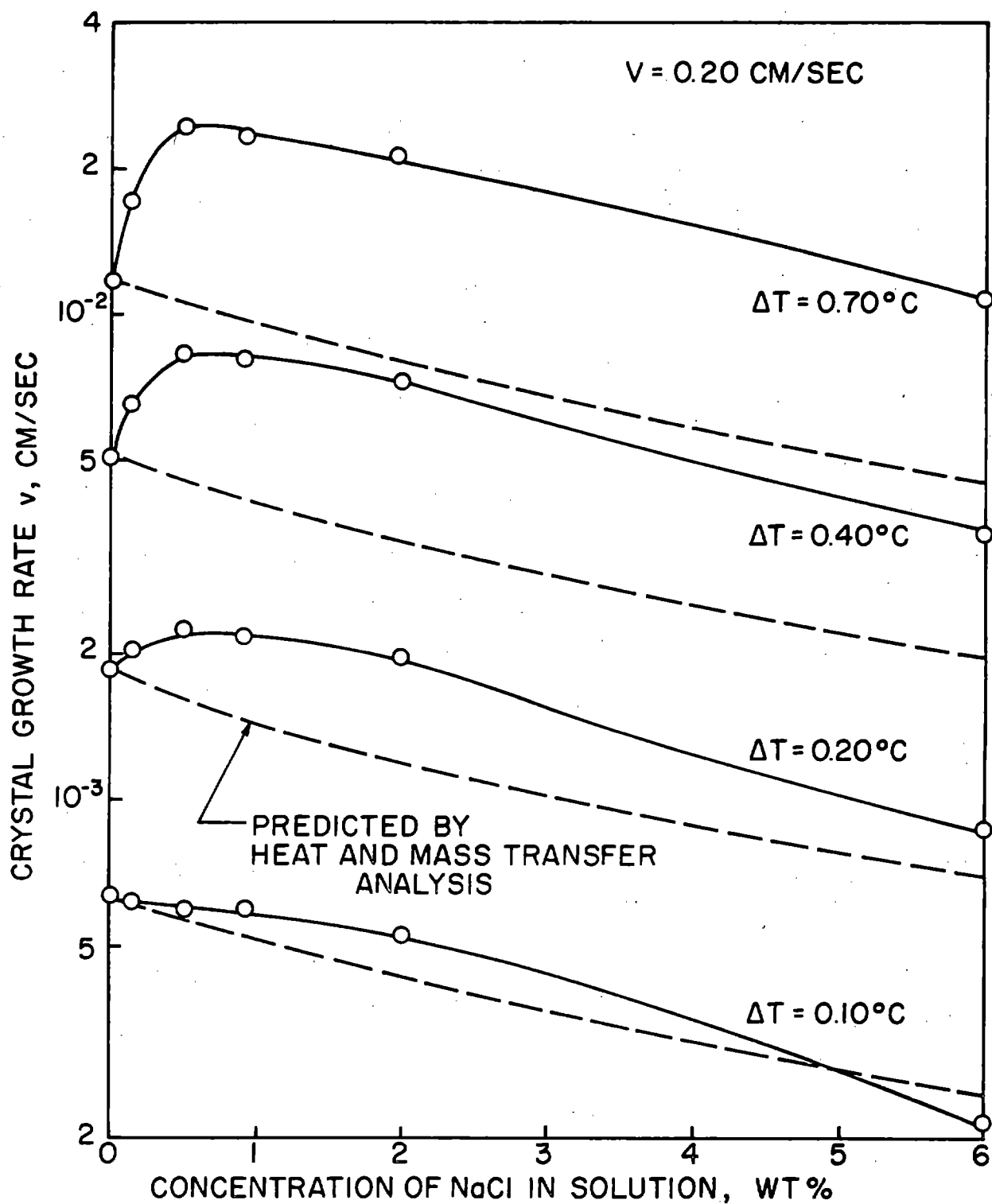


FIGURE 30 : ICE CRYSTAL GROWTH RATE VS. SOLUTION CONCENTRATION AS A FUNCTION OF SUBCOOLING: $V = 0.20 \text{ CM/SEC}$

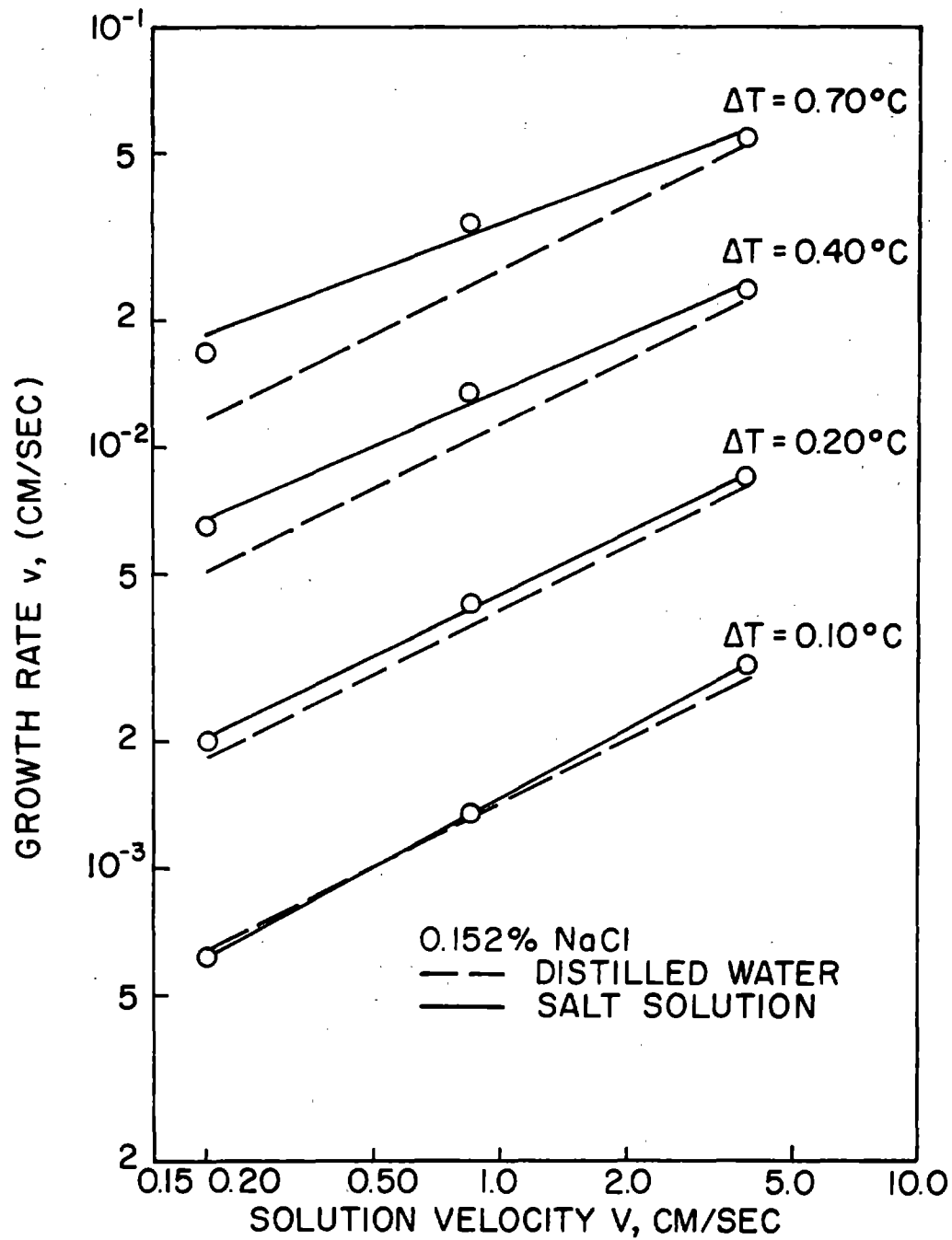


FIGURE 31 : ICE CRYSTAL GROWTH RATE VS. SOLUTION VELOCITY IN 0.152 WT. % NaCl SOLUTION WITH SUBCOOLING AS A PARAMETER

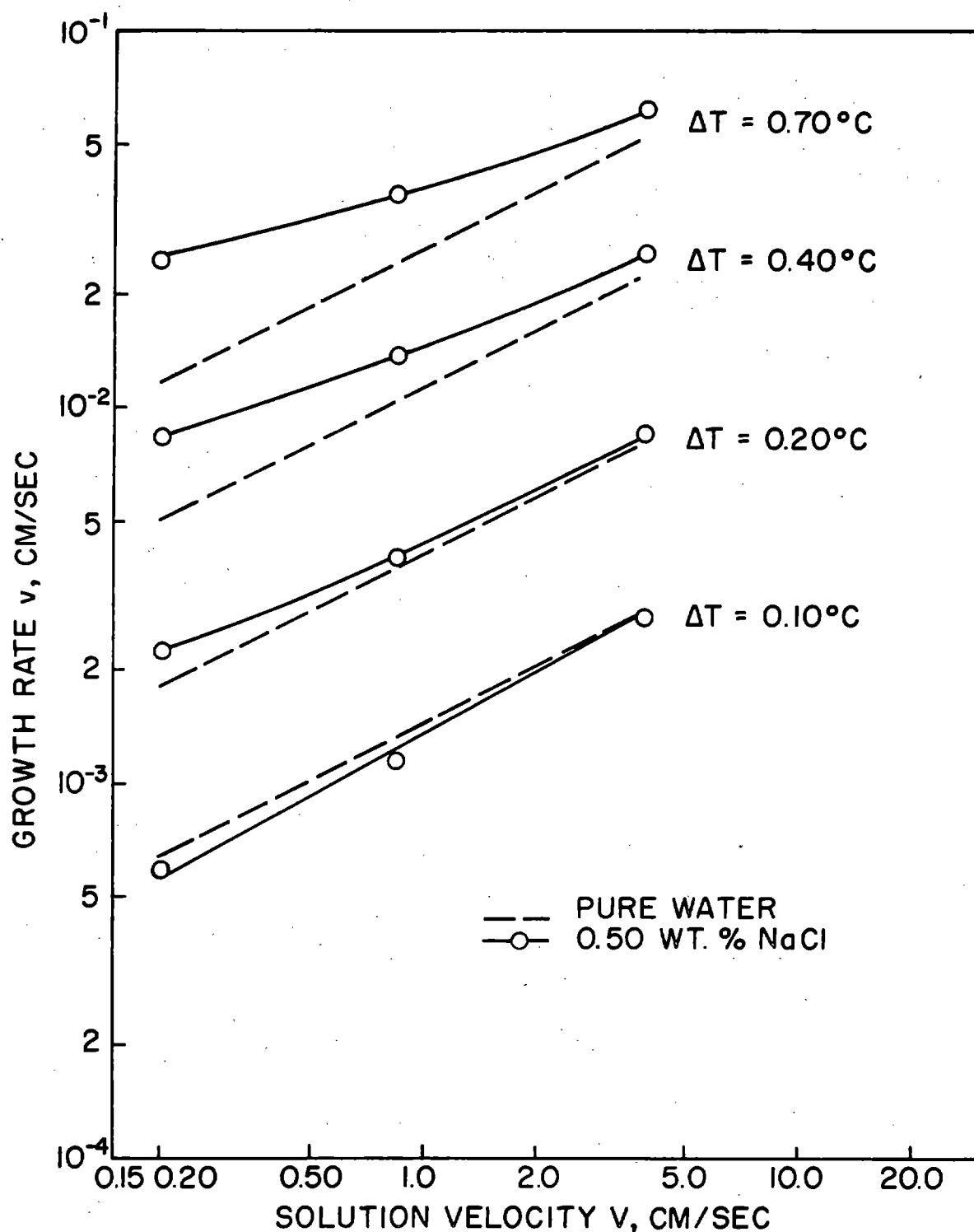


FIGURE 32 : ICE CRYSTAL GROWTH RATE VS. SOLUTION VELOCITY IN 0.50 WT. % NaCl SOLUTION WITH SUBCOOLING AS A PARAMETER

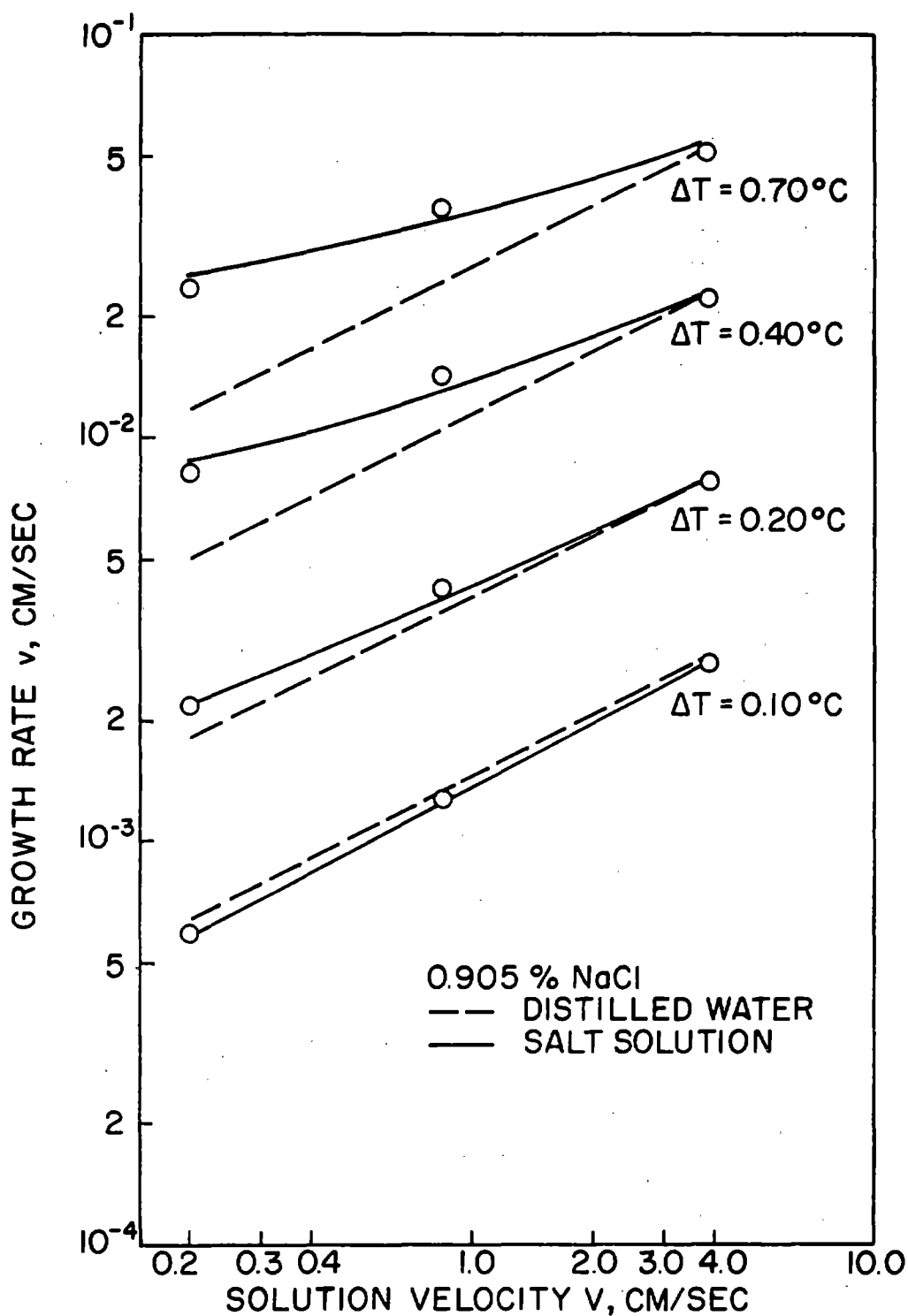


FIGURE 33 : ICE CRYSTAL GROWTH RATE VS. SOLUTION VELOCITY IN 0.905 WT. % NaCl SOLUTION WITH SUBCOOLING AS A PARAMETER

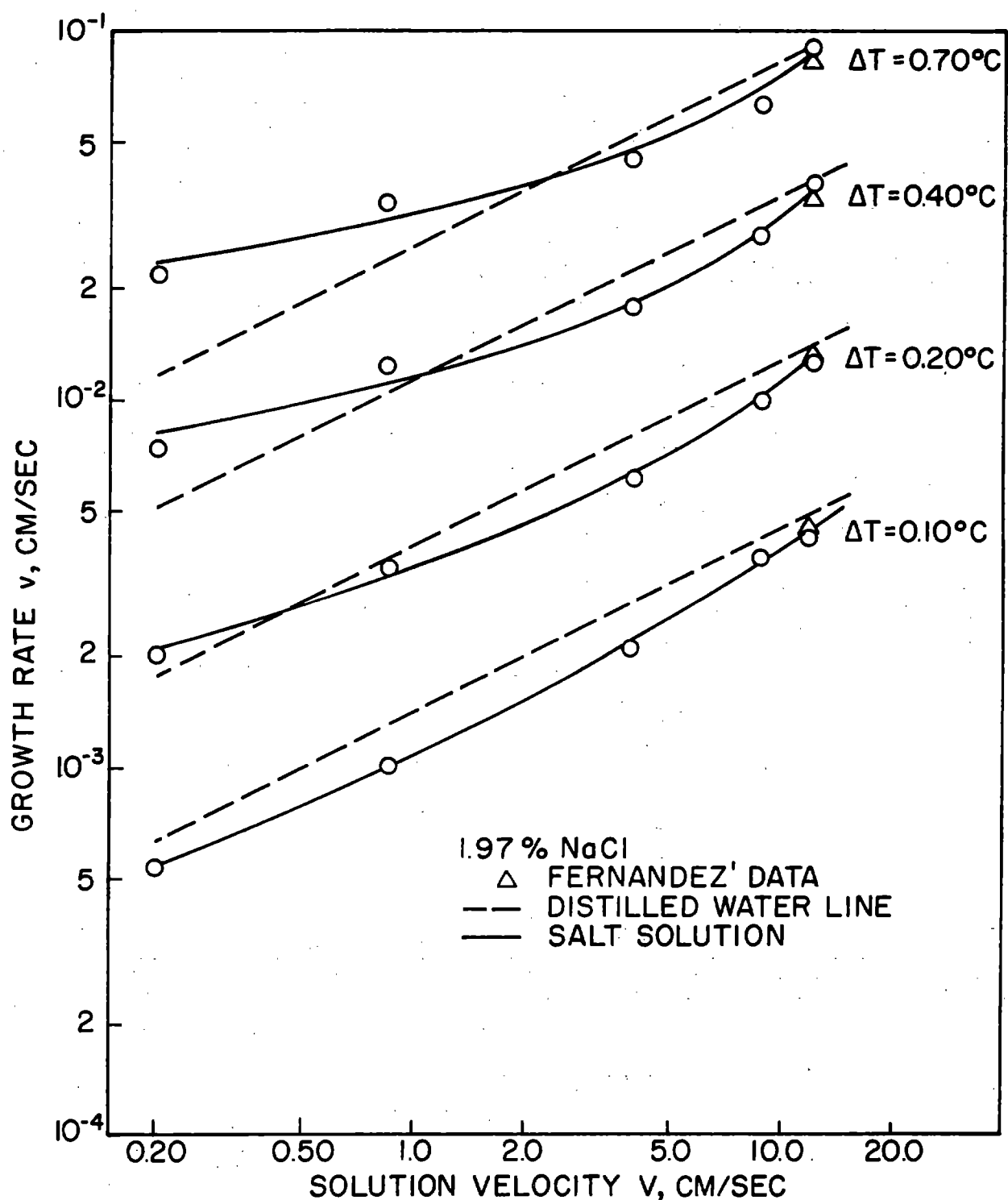


FIGURE 34 : ICE CRYSTAL GROWTH RATE VS. SOLUTION VELOCITY IN 1.97 % NaCl SOLUTION WITH SUBCOOLING AS A PARAMETER

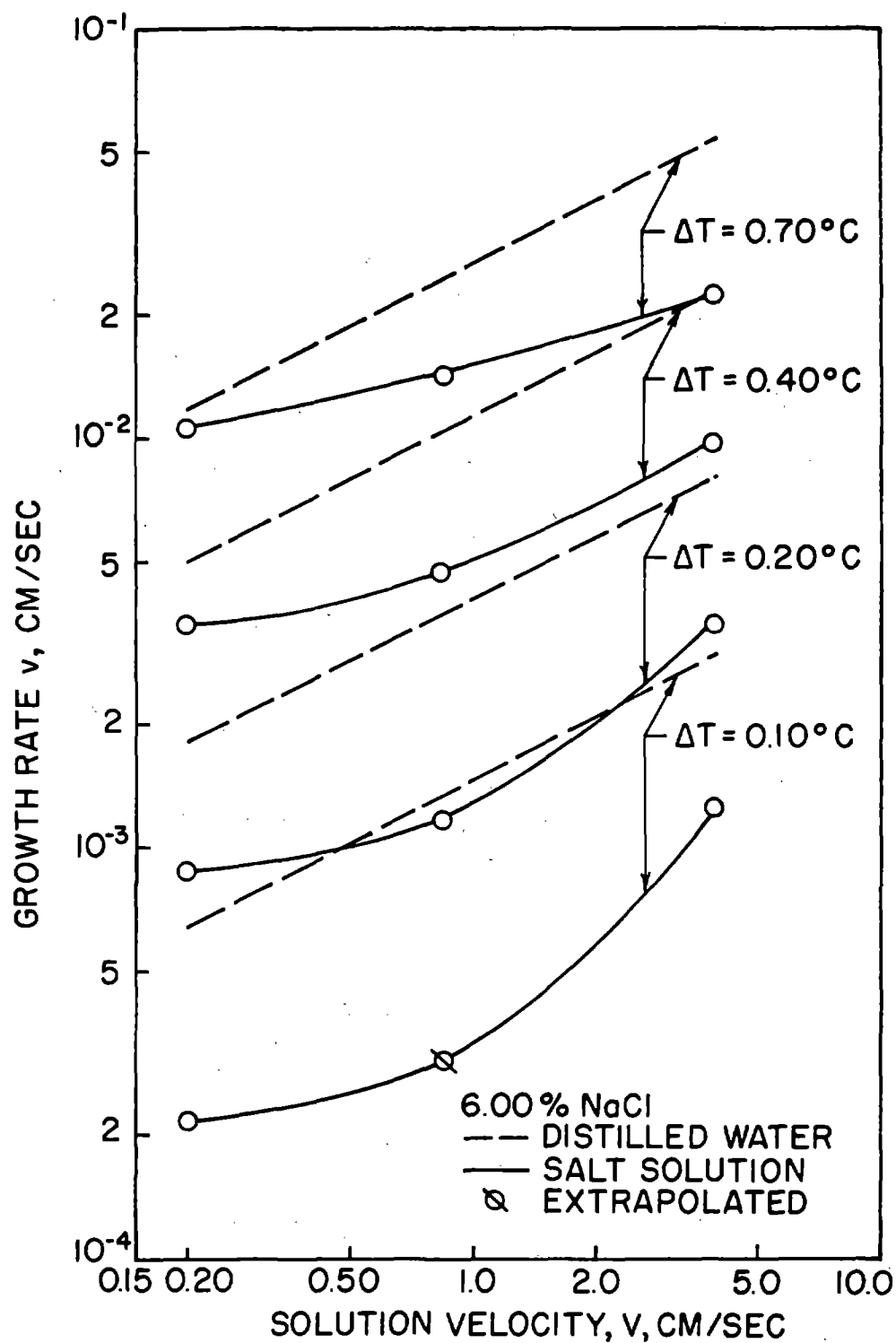


FIGURE 35 : ICE CRYSTAL GROWTH RATE VS. SOLUTION VELOCITY IN 6.00% NaCl SOLUTION WITH SUBCOOLING AS A PARAMETER

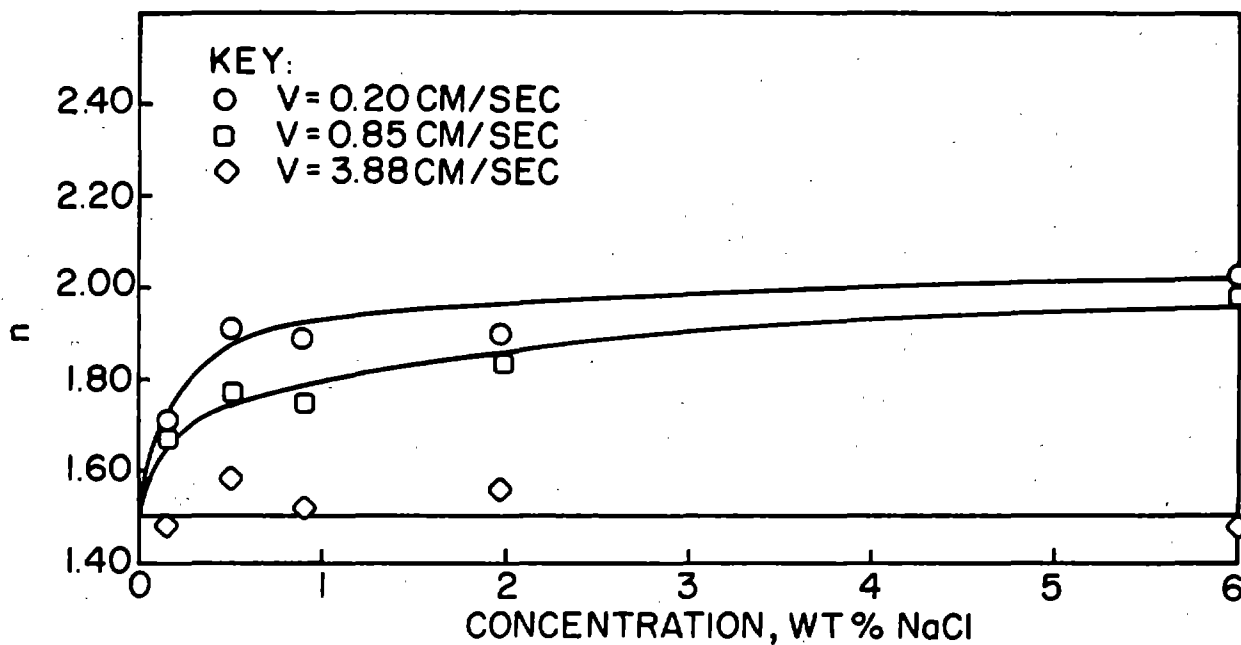


FIGURE 36 : VALUES OF n IN $v = a\Delta T^n$ VS. CONCENTRATION OF NaCl WITH SOLUTION VELOCITY AS A PARAMETER

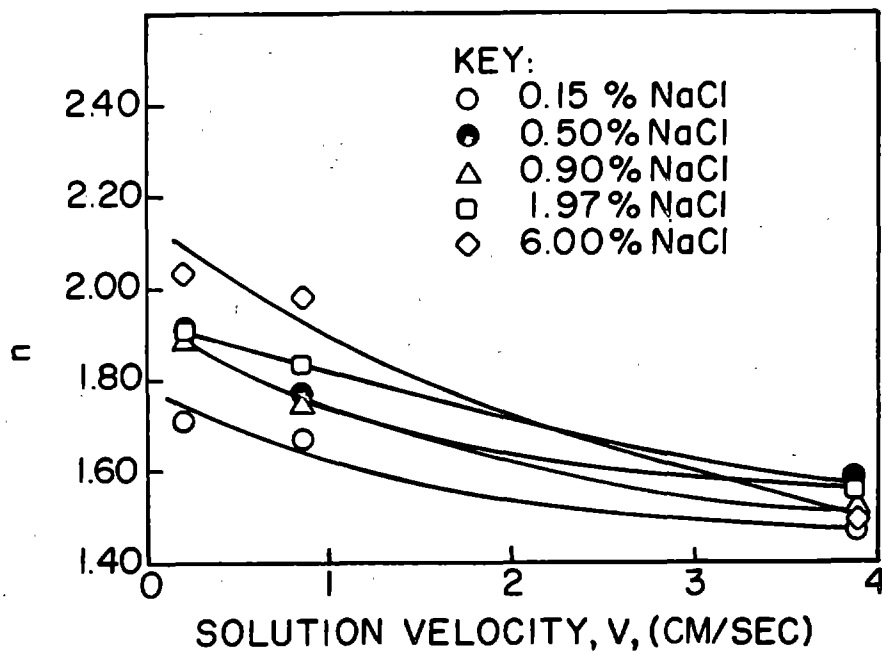


FIGURE 36A: VALUES OF n IN $v = a\Delta T^n$ VS. SOLUTION VELOCITY, V, (CM/SEC) WITH CONCENTRATION AS A PARAMETER

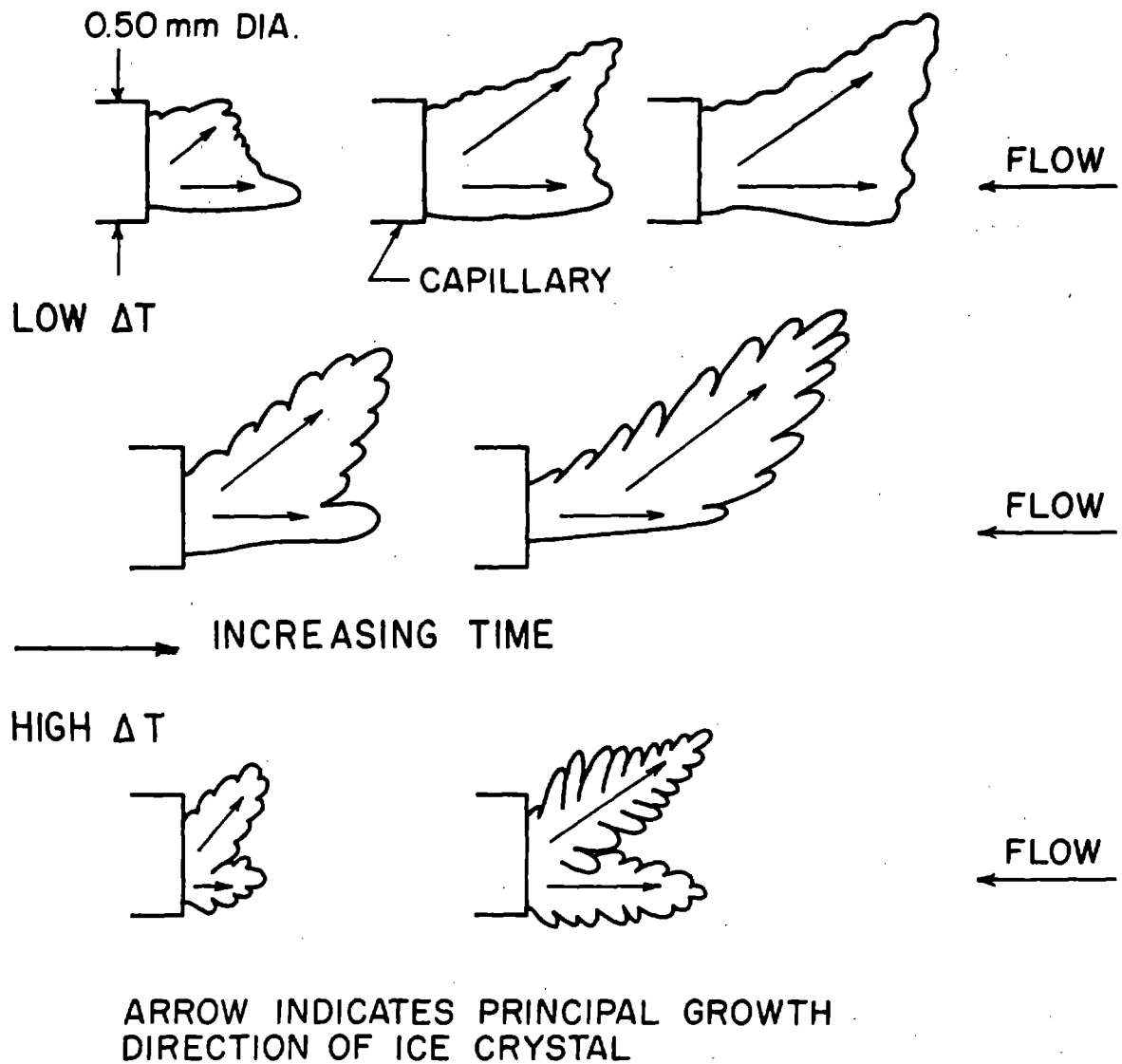


FIGURE 37 : ANOMALOUS ICE GROWTH BEHAVIOR
OBSERVED AT $V = 3.88 \text{ CM/SEC}$: 0.152%
 NaCl AND 1.97% NaCl

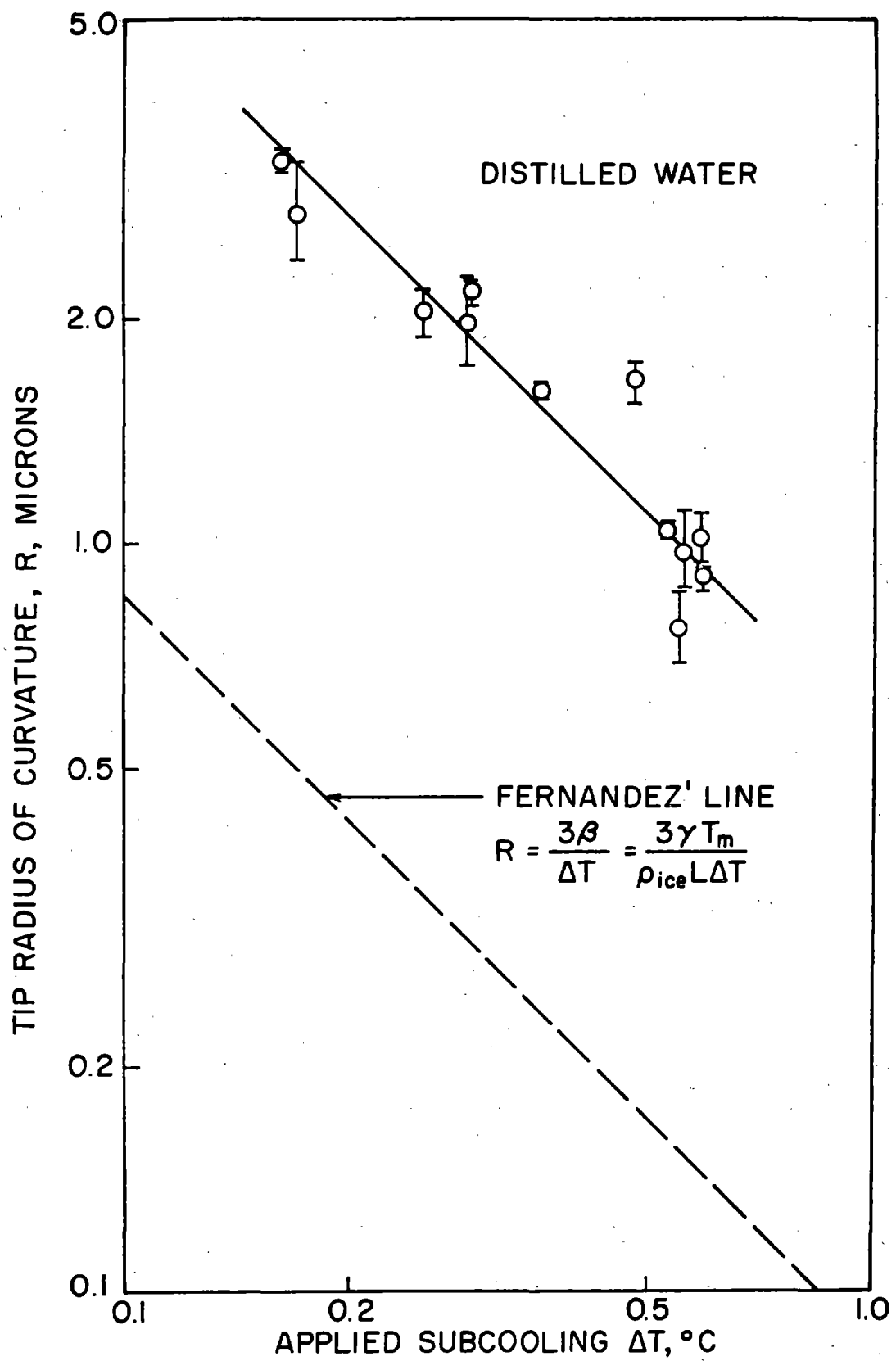


FIGURE 38: TIP RADIUS OF CURVATURE VS. APPLIED SUBCOOLING IN DISTILLED WATER

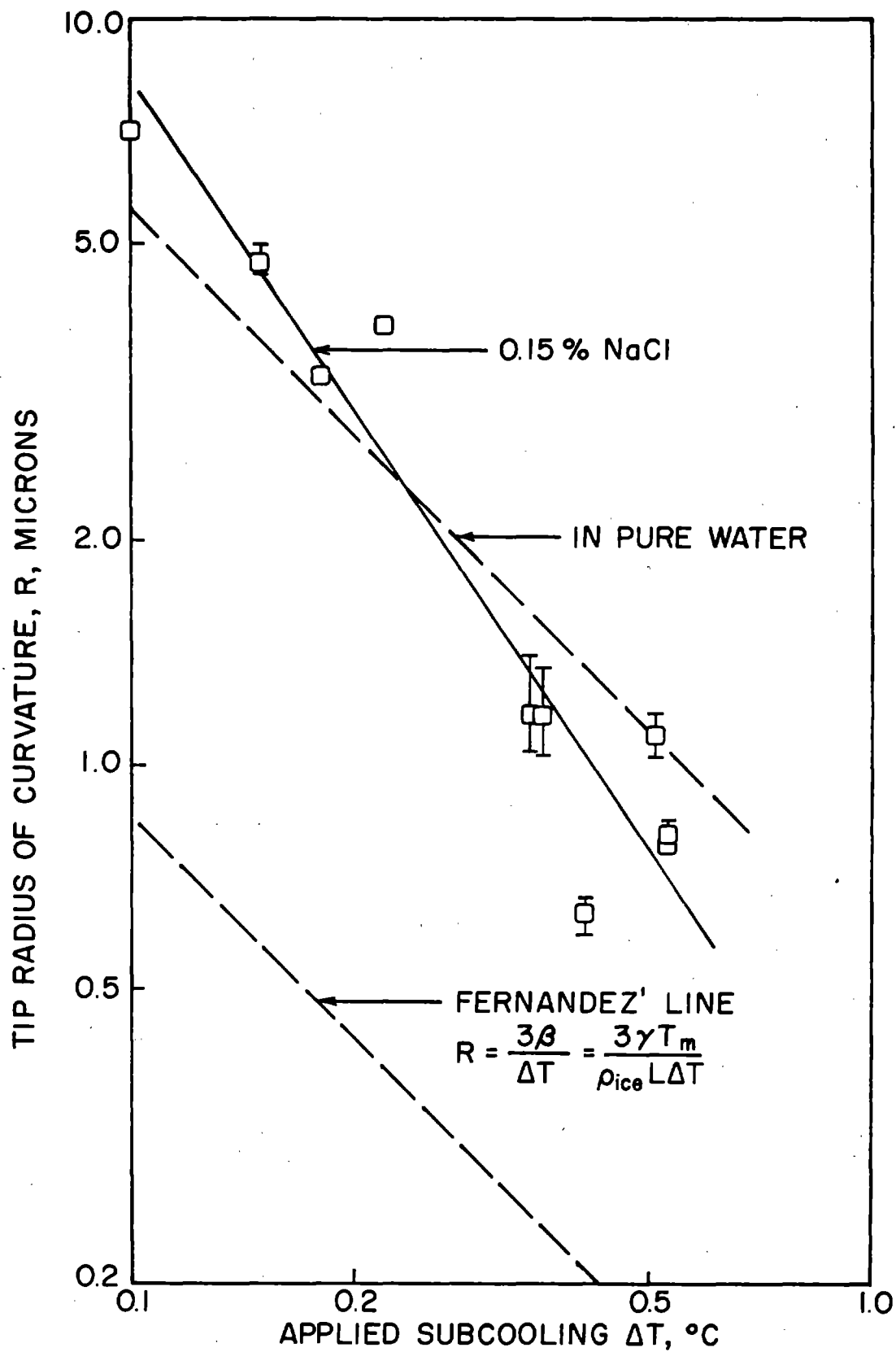


FIGURE 39 : TIP RADIUS OF CURVATURE VS. APPLIED SUBCOOLING IN 0.15 % NaCl SOLUTION

DISTILLED
WATER →



(A) $\Delta T = 0.16^\circ\text{C}$

0.25 mm

(B) $\Delta T = 0.55^\circ\text{C}$

0.15% NaCl
SOLUTION →



(C) $\Delta T = 0.10^\circ\text{C}$



(D) $\Delta T = 0.53^\circ\text{C}$

FIGURE 40: PHOTOGRAPHS OF GROWING ICE CRYSTALS
AT VARIOUS DEGREES OF SUBCOOLING:
EDGE VIEW

Reproduced from
best available copy.



$\Delta T = 0.43^{\circ}\text{C}$
DISTILLED WATER

Reproduced from
best available copy.

FIGURE 41: PHOTOGRAPH OF GROWING ICE CRYSTAL:
TOP VIEW

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written permission of the National Aeronautics and
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used to furnish the best available data to the
user.

TABLE 1
CONSTANTS IN THE EQUATION $v = a'\Delta T^n$ - DATA OF FERNANDEZ (1967)

Centerline Water Velocity V, cm/sec.	n	a'
46.0	1.45	0.295
20.0	1.48	0.203
13.5	1.52	0.173
8.0	1.55	0.150
3.0	1.74	0.132
1.52	1.67	0.059
1.30	1.82	0.073

TABLE 2
CONSTANTS IN THE EQUATION $v = a'\Delta T^n$ - DATA OF POISOT (1968)

Centerline Water Velocity V, cm/sec.	n	a'
16.0	1.46	0.138
8.0	1.48	0.096
2.18	1.49	0.053
1.00	1.50	0.040

TABLE 3
CONSTANTS IN THE EQUATION $v = a'\Delta T^n$ - DISTILLED WATER
DATA OF FARRAR AND HAMILTON (1965)

Water Velocity (cm/sec)	n	a'
29.0	1.72	0.282
16.1	1.68	0.243
10.0	1.45	0.171
1.78	1.45	0.077
0	2.04	0.0096

TABLE 4
CONSTANTS IN THE EQUATION $r = a' \Delta T^n$ - DISTILLED WATER
DATA OF HUIGE AND THIJSSSEN (1969)

Water Velocity	n	a'
21.2	1.51	0.158
17.4	1.54	0.157
14.6	1.48	0.168
10.2	1.60	0.152
6.00	1.58	0.149
3.10	1.38	0.095
1.79	1.46	0.072
0.80	1.05	0.032

TABLE 5
CONSTANTS IN THE EQUATION $v = a' \Delta T^n$ - FREE GROWTH OF
ICE CRYSTALS IN QUIESCENT DISTILLED WATER

Worker	n	a'	Subcooling Range
Lindenmeyer and Chalmers (1966)	2.39	0.023	2.0 - 6.5°C
Hallet (1964)	1.9	0.080	1.0 - 15°C
Farrar and Hamilton (1965)	2.04	0.0096	0.03 - 1.02°C
Pruppacher (1967)	2.22	0.035	0.5 - 9°C
Huige and Thijssen (1969)	2.22	0.030	0.9 - 5°C

TABLE 6
EXPERIMENTAL DATA IN DISTILLED WATER-ICE CRYSTAL GROWTH RATES

Centerline Water Velocity V (cm/sec)	Subcooling $\Delta T(^{\circ}\text{C})$	Growth Rate v (cm/sec)	Centerline Water Velocity V (cm/sec)	Subcooling $\Delta T(^{\circ}\text{C})$	Growth Rate v (cm/sec)
1.00	0.20	3.67×10^{-3}	0.50	0.56	1.41×10^{-2}
	0.23	4.76×10^{-3}		0.56	1.46×10^{-2}
	0.23	5.19×10^{-3}		0.56	1.47×10^{-2}
	0.25	4.95×10^{-3}		0.59	1.58×10^{-2}
	0.30	7.07×10^{-3}		0.59	1.61×10^{-2}
	0.30	7.15×10^{-3}		0.77	2.50×10^{-2}
	0.49	1.62×10^{-2}		0.78	2.62×10^{-2}
	0.65	2.42×10^{-2}		0.80	2.63×10^{-2}
	0.77	3.04×10^{-2}		0.87	2.89×10^{-2}
0.50	0.08	8.00×10^{-4}	0.22	0.14	1.34×10^{-3}
	0.11	1.03×10^{-3}		0.15	1.30×10^{-3}
	0.14	1.54×10^{-3}		0.16	1.50×10^{-3}
	0.16	1.80×10^{-3}		0.22	2.02×10^{-3}
	0.17	2.12×10^{-3}		0.23	2.01×10^{-3}
	0.18	2.52×10^{-3}		0.26	2.95×10^{-3}
	0.18	2.62×10^{-3}		0.35	4.99×10^{-3}
	0.19	2.42×10^{-3}		0.42	6.40×10^{-3}
	0.19	2.66×10^{-3}		0.44	6.90×10^{-3}
	0.21	3.04×10^{-3}		0.45	6.48×10^{-3}
	0.21	3.26×10^{-3}		0.47	7.29×10^{-3}
	0.22	2.84×10^{-3}		0.49	8.31×10^{-3}
	0.22	2.96×10^{-3}		0.50	7.60×10^{-3}
	0.22	3.11×10^{-3}		0.52	8.94×10^{-3}
	0.24	3.44×10^{-3}		0.54	9.06×10^{-3}
	0.26	4.19×10^{-3}		0.56	8.91×10^{-3}
	0.26	4.60×10^{-3}			
	0.27	4.43×10^{-3}			
	0.29	5.16×10^{-3}			
	0.37	7.43×10^{-3}			
	0.38	6.64×10^{-3}			
	0.44	1.07×10^{-2}			
			(Continued)		

TABLE 6 (Cont'd.)
EXPERIMENTAL DATA IN DISTILLED WATER-ICE CRYSTAL GROWTH RATES

Centerline Water Velocity V (cm/sec)	Subcooling $\Delta T(^{\circ}\text{C})$	Growth Rate v (cm/sec)	Centerline Water Velocity V (cm/sec)	Subcooling $\Delta T(^{\circ}\text{C})$	Growth Rate v (cm/sec)
0.11	0.16	9.00×10^{-4}	0.042	0.45	2.90×10^{-3}
	0.18	1.19×10^{-3}		0.49	3.02×10^{-3}
	0.19	1.11×10^{-3}		0.49	3.09×10^{-3}
	0.20	1.33×10^{-3}			
	0.23	1.55×10^{-3}			
	0.23	2.10×10^{-3}			
	0.29	2.53×10^{-3}			
	0.30	2.37×10^{-3}			
	0.35	3.12×10^{-3}			
	0.36	3.15×10^{-3}			
	0.37	3.50×10^{-3}			
0.042	0.40	3.88×10^{-3}			
	0.48	5.30×10^{-3}			
	0.57	6.18×10^{-3}			
	0.13	4.60×10^{-4}			
	0.14	3.90×10^{-4}			
	0.22	9.33×10^{-4}			
	0.23	9.10×10^{-4}			
	0.24	1.00×10^{-3}			
	0.24	1.04×10^{-3}			
	0.24	1.27×10^{-3}			
	0.26	1.22×10^{-3}			
	0.28	1.20×10^{-3}			
	0.28	1.30×10^{-3}			
	0.29	1.30×10^{-3}			
	0.33	1.50×10^{-3}			
	0.36	1.77×10^{-3}			
	0.37	1.90×10^{-3}			
	0.41	2.16×10^{-3}			

TABLE 7
CONSTANTS IN THE EQUATION $v = a' \Delta T^n$ - DISTILLED WATER

Centerline Water Velocity V(cm/sec)	n	a'
1.00	1.58	0.048
0.50	1.59	0.036
0.22	1.51	0.023
0.11	1.50	0.015
0.042	1.50	0.0087
Units: v(cm/sec); $\Delta T(^{\circ}\text{C})$		

TABLE 8
CONSTANT IN THE EQUATION $v = a' \Delta T^{3/2}$ - DISTILLED WATER

Centerline Water Velocity V(cm/sec)	a'
1.00	0.044
0.50	0.032
0.22	0.023
0.11	0.015
0.042	0.0087

TABLE 9
EXPERIMENTAL DATA IN SALT SOLUTION - ICE CRYSTAL GROWTH RATES
SOLUTION CONCENTRATION = 0.152 Wt. % NaCl

Centerline Solution Velocity V(cm/sec)	Subcooling $\Delta T(^{\circ}\text{C})$	Growth Rate v(cm/sec)	Centerline Solution Velocity V(cm/sec)	Subcooling $\Delta T(^{\circ}\text{C})$	Growth Rate v(cm/sec)
0.20	0.08	4.63×10^{-4}	0.85	0.35	1.13×10^{-2}
	0.14	1.38×10^{-3}		0.36	1.20×10^{-2}
	0.19	1.72×10^{-3}		0.38	1.31×10^{-2}
	0.20	1.93×10^{-3}		0.38	1.41×10^{-2}
	0.22	2.24×10^{-3}		0.43	1.56×10^{-2}
	0.26	2.55×10^{-3}		0.45	1.70×10^{-2}
	0.27	2.80×10^{-3}		0.49	2.14×10^{-2}
	0.27	2.70×10^{-3}		0.52	2.19×10^{-2}
	0.29	3.36×10^{-3}		0.55	2.45×10^{-2}
	0.44	7.39×10^{-3}		0.57	2.68×10^{-2}
0.85	0.51	1.11×10^{-2}		0.64	3.03×10^{-2}
	0.59	1.28×10^{-2}		0.64	3.15×10^{-2}
	0.59	1.41×10^{-2}		0.73	3.50×10^{-2}
	0.72	1.88×10^{-2}		0.77	3.57×10^{-2}
	0.92	3.32×10^{-2}		0.78	4.35×10^{-2}
	0.11	1.42×10^{-3}		0.88	4.45×10^{-2}
	0.11	1.33×10^{-3}		0.89	4.52×10^{-2}
	0.12	2.17×10^{-3}		0.89	5.52×10^{-2}
	0.15	2.68×10^{-3}		0.92	4.73×10^{-2}
	0.15	2.07×10^{-3}		0.94	4.75×10^{-2}
	0.16	3.13×10^{-3}		0.95	6.38×10^{-2}
	0.18	3.80×10^{-3}		0.98	6.02×10^{-2}
	0.20	4.00×10^{-3}			
	0.20	4.05×10^{-3}			
	0.22	4.27×10^{-3}			
	0.22	4.70×10^{-3}			
	0.24	6.02×10^{-3}			
	0.34	1.05×10^{-2}			
	0.35	1.03×10^{-2}			

(Continued)

TABLE 9 (Cont'd.)
 EXPERIMENTAL DATA IN SALT SOLUTION - ICE CRYSTAL GROWTH RATES
 SOLUTION CONCENTRATION = 0.152 Wt.% NaCl

Centerline Solution Velocity V(cm/sec)	Subcooling $\Delta T(^{\circ}\text{C})$	Growth Rate v(cm/sec)
3.88	0.18	7.00×10^{-3}
	0.37	1.94×10^{-2}
	0.39	2.52×10^{-2}
	0.51	3.41×10^{-2}
	0.52	3.20×10^{-2}
	0.58	4.70×10^{-2}
	0.67	5.29×10^{-2}
	0.69	4.86×10^{-2}
	0.70	6.71×10^{-2}
	0.73	5.10×10^{-2}
	0.73	5.23×10^{-2}

TABLE 10
EXPERIMENTAL DATA IN SALT SOLUTION - ICE CRYSTAL GROWTH RATES
SOLUTION CONCENTRATION = 0.502 Wt.% NaCl

Centerline Solution Velocity V (cm/sec)	Subcooling $\Delta T(^{\circ}C)$	Growth Rate v (cm/sec)	Centerline Solution Velocity v (cm/sec)	Subcooling $\Delta T(^{\circ}C)$	Growth Rate v (cm/sec)
0.20	0.07	3.21×10^{-4}	0.85	0.32	1.03×10^{-2}
	0.08	5.48×10^{-4}		0.36	1.00×10^{-2}
	0.12	8.09×10^{-4}		0.39	1.54×10^{-2}
	0.13	8.28×10^{-4}		0.45	1.83×10^{-2}
	0.17	1.46×10^{-3}		0.47	2.37×10^{-2}
	0.22	2.37×10^{-3}		0.48	1.92×10^{-2}
	0.22	2.12×10^{-3}		0.48	2.15×10^{-2}
	0.23	2.61×10^{-3}		0.49	1.92×10^{-2}
	0.26	2.90×10^{-3}		0.53	1.87×10^{-2}
	0.27	4.02×10^{-3}		0.55	2.52×10^{-2}
0.85	0.36	6.75×10^{-3}	3.88	0.57	2.43×10^{-2}
	0.37	6.88×10^{-3}		0.64	3.13×10^{-2}
	0.45	1.09×10^{-2}		0.65	3.35×10^{-2}
	0.53	1.64×10^{-2}		0.05	1.07×10^{-3}
	0.57	1.72×10^{-2}		0.06	1.21×10^{-3}
	0.64	2.48×10^{-2}		0.10	3.37×10^{-3}
	0.76	2.86×10^{-2}		0.11	3.20×10^{-3}
	0.90	4.36×10^{-2}		0.16	4.46×10^{-3}
	0.09	1.04×10^{-3}		0.18	5.70×10^{-3}
	0.11	1.56×10^{-3}		0.25	1.14×10^{-2}
0.85	0.14	1.93×10^{-3}	3.88	0.31	1.51×10^{-2}
	0.17	2.88×10^{-3}		0.37	2.69×10^{-2}
	0.20	4.23×10^{-3}		0.45	3.18×10^{-2}
	0.22	4.45×10^{-3}		0.45	3.40×10^{-2}
	0.24	5.47×10^{-3}		0.53	3.89×10^{-2}
	0.27	6.86×10^{-3}		0.57	4.94×10^{-2}
	0.29	7.84×10^{-3}		0.60	4.82×10^{-2}
	0.30	7.81×10^{-3}		0.62	5.66×10^{-2}
	0.32	7.93×10^{-3}		0.67	5.73×10^{-2}
				0.76	7.02×10^{-2}

TABLE 11
EXPERIMENTAL DATA IN SALT SOLUTION - ICE CRYSTAL GROWTH RATES
SOLUTION CONCENTRATION = 0.905 Wt. % NaCl

Centerline Solution Velocity V (cm/sec)	Subcooling $\Delta T(^{\circ}C)$	Growth Rate v (cm/sec)	Centerline Solution Velocity V (cm/sec)	Subcooling $\Delta T(^{\circ}C)$	Growth Rate v (cm/sec)
0.20	0.11	6.95×10^{-4}	0.85	0.20	4.07×10^{-3}
	0.11	6.74×10^{-4}		0.22	5.63×10^{-3}
	0.13	1.20×10^{-3}		0.25	6.62×10^{-3}
	0.14	1.13×10^{-3}		0.26	6.71×10^{-3}
	0.15	1.01×10^{-3}		0.30	8.68×10^{-3}
	0.16	1.28×10^{-3}		0.31	1.09×10^{-2}
	0.17	1.83×10^{-3}		0.31	9.76×10^{-3}
	0.19	2.08×10^{-3}		0.40	1.47×10^{-2}
	0.23	2.89×10^{-3}		0.40	1.20×10^{-2}
	0.24	2.70×10^{-3}			
0.85	0.27	3.39×10^{-3}	3.88	0.10	2.44×10^{-3}
	0.28	4.10×10^{-3}		0.12	3.44×10^{-3}
	0.42	9.89×10^{-3}		0.13	4.09×10^{-3}
	0.42	8.35×10^{-3}		0.13	3.88×10^{-3}
	0.69	2.32×10^{-2}		0.18	7.77×10^{-3}
	0.71	2.26×10^{-2}		0.19	7.45×10^{-3}
	0.74	2.54×10^{-2}		0.26	8.56×10^{-3}
				0.53	3.53×10^{-2}
	0.41	1.68×10^{-2}		0.58	3.86×10^{-2}
	0.42	1.82×10^{-2}		0.72	5.41×10^{-2}
	0.48	2.01×10^{-2}		0.74	5.44×10^{-2}
	0.52	2.23×10^{-2}			
	0.56	2.19×10^{-2}			
	0.62	2.74×10^{-2}			
	0.65	2.94×10^{-2}			
	0.10	1.55×10^{-3}			
	0.12	1.31×10^{-3}			
	0.13	1.65×10^{-3}			
	0.14	3.32×10^{-3}			

TABLE 12
EXPERIMENTAL DATA IN SALT SOLUTION - ICE CRYSTAL GROWTH RATES
SOLUTION CONCENTRATION = 1.97 Wt.% NaCl

Centerline Solution Velocity V (cm/sec)	Subcooling $\Delta T(^{\circ}\text{C})$	Growth Rate v (cm/sec)	Centerline Solution Velocity V (cm/sec)	Subcooling $\Delta T(^{\circ}\text{C})$	Growth Rate v (cm/sec)
0.20	0.09	4.39×10^{-4}	3.88	0.20	6.00×10^{-3}
	0.09	3.68×10^{-4}		0.28	1.20×10^{-2}
	0.10	5.62×10^{-4}		0.30	1.05×10^{-2}
	0.20	2.24×10^{-3}		0.32	1.47×10^{-2}
	0.22	2.63×10^{-3}		0.36	1.53×10^{-2}
	0.29	4.84×10^{-3}		0.36	1.31×10^{-2}
	0.34	5.43×10^{-3}		0.38	1.84×10^{-2}
	0.37	6.61×10^{-3}		0.42	1.77×10^{-2}
	0.42	8.40×10^{-3}		0.49	2.25×10^{-2}
	0.47	1.07×10^{-2}		0.50	2.40×10^{-2}
	0.48	8.85×10^{-3}		0.52	2.35×10^{-2}
	0.52	1.26×10^{-2}		0.52	2.62×10^{-2}
	0.52	1.26×10^{-2}		0.53	3.09×10^{-2}
	0.53	1.25×10^{-2}		0.53	2.86×10^{-2}
	0.62	1.40×10^{-2}		0.54	3.02×10^{-2}
0.85	0.13	1.72×10^{-3}	8.85	0.56	2.94×10^{-2}
	0.14	2.15×10^{-3}		0.59	3.52×10^{-2}
	0.19	3.02×10^{-3}		0.60	4.14×10^{-2}
	0.19	2.70×10^{-3}		0.65	3.53×10^{-2}
	0.20	3.07×10^{-3}		0.70	4.44×10^{-2}
	0.22	3.96×10^{-3}			
	0.27	5.21×10^{-3}		0.04	1.27×10^{-3}
	0.36	1.17×10^{-2}		0.07	1.46×10^{-3}
	0.41	1.63×10^{-2}		0.07	2.38×10^{-3}
	0.45	1.82×10^{-2}		0.22	1.05×10^{-2}
	0.46	1.66×10^{-2}		0.31	1.75×10^{-2}
	0.47	1.40×10^{-2}		0.34	2.20×10^{-2}
	0.51	1.86×10^{-2}		0.37	2.46×10^{-2}
	0.61	2.77×10^{-2}		0.42	3.17×10^{-2}
				0.55	4.66×10^{-2}

(Continued)

TABLE 12 (Cont'd.)
 EXPERIMENTAL DATA IN SALT SOLUTION - ICE CRYSTAL GROWTH RATES
 SOLUTION CONCENTRATION = 1.97 Wt. % NaCl

Centerline Solution Velocity V(cm/sec)	Subcooling $\Delta T(^{\circ}\text{C})$	Growth Rate v(cm/sec)
11.9	0.04	1.18×10^{-3}
	0.07	2.38×10^{-3}
	0.10	4.43×10^{-3}
	0.10	3.08×10^{-3}
	0.11	3.97×10^{-3}
	0.17	1.10×10^{-2}
	0.18	1.09×10^{-2}
	0.20	1.38×10^{-2}
	0.24	1.77×10^{-2}
	0.28	1.95×10^{-2}
	0.29	2.30×10^{-2}
	0.29	2.26×10^{-2}
	0.29	2.11×10^{-2}
	0.29	2.45×10^{-2}
	0.31	2.28×10^{-2}
	0.36	2.82×10^{-2}
	0.54	7.34×10^{-2}

TABLE 13
EXPERIMENTAL DATA IN SALT SOLUTION - ICE CRYSTAL GROWTH RATES
SOLUTION CONCENTRATION = 6.00 Wt.% NaCl

Centerline Solution Velocity V(cm/sec)	Subcooling $\Delta T(^{\circ}C)$	Growth Rate v(cm/sec)	Centerline Solution Velocity V(cm/sec)	Subcooling $\Delta T(^{\circ}C)$	Growth Rate v(cm/sec)
0.20	0.11	1.56×10^{-4}	0.85	0.23	1.54×10^{-3}
	0.13	4.71×10^{-4}		0.27	2.22×10^{-3}
	0.16	4.00×10^{-4}		0.28	2.16×10^{-3}
	0.18	7.75×10^{-4}		0.37	4.48×10^{-3}
	0.18	9.45×10^{-4}		0.38	4.26×10^{-3}
	0.19	8.75×10^{-4}		0.42	5.86×10^{-3}
	0.19	8.06×10^{-4}		0.48	5.66×10^{-3}
	0.23	1.16×10^{-3}		0.53	7.57×10^{-3}
	0.23	1.37×10^{-3}		0.56	7.79×10^{-2}
	0.25	1.26×10^{-3}		0.66	1.46×10^{-2}
	0.26	1.42×10^{-3}			
	0.27	1.31×10^{-3}	3.88	0.17	2.64×10^{-3}
	0.29	2.00×10^{-3}		0.33	7.76×10^{-3}
	0.30	1.50×10^{-3}		0.34	7.60×10^{-3}
	0.32	2.38×10^{-3}		0.41	9.75×10^{-3}
	0.32	2.51×10^{-3}		0.46	1.14×10^{-2}
	0.33	2.52×10^{-3}		0.46	1.16×10^{-2}
	0.42	4.80×10^{-3}		0.48	1.27×10^{-2}
	0.46	3.86×10^{-3}		0.48	1.29×10^{-2}
	0.46	4.12×10^{-3}		0.55	1.74×10^{-2}
	0.48	4.75×10^{-3}		0.73	2.27×10^{-2}

TABLE 14
EXPERIMENTAL DATA IN GLUCOSE SOLUTION
SOLUTION CONCENTRATION = 1.53 Wt. %

Centerline Solution Velocity V(cm/sec)	Subcooling $\Delta T(^{\circ}\text{C})$	Growth Rate v(cm/sec)
0.64	0.31	8.46×10^{-3}
	0.32	9.28×10^{-3}
	0.46	1.46×10^{-2}
	0.53	1.87×10^{-2}
	0.56	2.10×10^{-2}
	0.58	1.96×10^{-2}
	0.62	2.05×10^{-2}

TABLE 15
VALUES OF n IN $v = a' \Delta T^n$ AS A FUNCTION OF
NaCl CONCENTRATION AND SOLUTION VELOCITY

Solution Velocity, V cm/sec	Weight Per Cent NaCl in Solution					
	0	0.152	0.502	0.905	1.97	6.00
0.20	(1.50)	1.71	1.91	1.89	1.90	2.03
0.85	(1.50)	1.67	1.77	1.75	1.83	1.98
3.88	(1.50)	1.48	1.59	1.52	1.56	1.49
8.85	(1.50)				1.47	
11.9	(1.50)				1.59	

TABLE 16
VALUES OF a' IN $v = a' \Delta T^n$ AS A FUNCTION OF
NaCl CONCENTRATION AND SOLUTION VELOCITY

Solution Velocity, V cm/sec	Weight Per Cent NaCl Solution				
	0.152	0.502	0.905	1.97	6.00
0.20	0.032	0.048	0.045	0.042	0.022
0.85	0.062	0.070	0.071	0.067	0.028
3.88	0.092	0.11	0.088	0.076	0.038
8.85				0.11	
11.9				0.16	

TABLE 17
EXPERIMENTAL DATA OF TIP RADIUS OF CURVATURE
VS. APPLIED SUBCOOLING

Distilled Water		0.15% NaCl Solution	
$\Delta T, ^\circ C$	R, microns	$\Delta T, ^\circ C$	R, microns
0.16	3.3	0.10	7.0
0.17	2.8	0.15	4.8
0.25	2.0	0.18	3.3
0.29	2.2	0.22	3.9
0.29	2.0	0.35	1.2
0.36	1.6	0.36	1.2
0.48	1.7	0.41	0.6
0.53	1.0	0.51	1.1
0.55	0.8	0.53	0.8
0.56	1.0	0.53	0.8
0.59	1.0		
0.59	0.9		