THE SPECIFIC HEAT OF SALINE ICE

by

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ABSTRACT

A calorimetric experiment was performed to empirically determine the variation of the specific heat of saline ice with respect to temperature for different salinities. The temperature range studied was from -23°C to the melting point of the salty ice. The salinity of these samples varied from $0^{\circ}/oo$ to $10^{\circ}/oo$. The experimental results seem to agree with the theoretical model determined by Schwerdtfeger for calculating the specific heat.

RESUME

La variation de la chaleur spécifique de la glace salée par rapport à la température est déterminée empériquement par une méthode calorimétrique.

La gamme de température étudiée s'étend de $-23^{\circ}C$ au point de fonte de la glace. La salinité de la glace est aussi variée de $0^{o}/oo$ à $10^{o}/oo$.

Les résultats semblent être en accord avec ceux prévus par le modèle de Schwerdtfeger qui calcule la chaleur spécifique d'une façon théorique.

ACKNOWLEDGEMENTS

Unfortunately, acknowledgements are meant to be short and to the point; in keeping with a certain tradition I suspect. Therefore rather than incur the wrath of some outraged printer or reader, let me begin. First I wish to sincerely thank my supervisor, Dr. E.R. Pounder, for directing my attention to this subject and for guidance in my project. I would also like to thank Dr. M.P. Langleben for valuable assistance. And I wish to extend to my colleagues in the Ice Physics Research group (namely Brian Wright, Eric Berger, Franz Goette, George Ostoich, Kevin Callaghan and Vladimir Koutitonsky) many thanks for criticism and moral support.

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Chapter 1 - Introduction

1.1 - Definition

In defining the specific heat of a system we start with a system whose initial state can be described by its temperature T and some other parameter (or set of parameters) x. For instance the restraining parameters can be volume, pressure etc. An infinitesimal amount of heat $đQ$ is now added to this system, keeping all parameters x fixed. As a result of this addition of heat there will be a change dT in the temperature of the system, which depends on the initial temperature T and the parameters defining its initial state. Then the ratio

$$C_x = \frac{1}{m} \frac{đQ}{dT}\bigg|_x$$

as $đQ \longrightarrow 0$

is called the specific heat of the substance. The subscript x denotes the parameters kept constant while adding the heat $đQ$. m denotes the mass of the substance considered so that the specific heat of the substance investigated is the function of the property of the material and not on the amount of material present. In this study the parameter held constant is pressure. The units to be used in this paper are the c.g.s units thus the specific heat will have the dimensions of calories per gram per degree celsius (cal/gm^{o}c).

In the above discussion the heat supplied to the system was purely for raising the temperature of the sample from its initial temperature T to some final temperature T + dT. However, in a substance like sea ice, supplying heat not only raises the temperature of the ice but there is some phase transition involved. Pounder (1965) in talking about the model of ice says "that the sea ice in its natural state always contains cells or pockets of brine, and any change of the temperature of the ice will involve a phase change of some of the water substance. That is to say water will become ice if the temperature is lowered or ice will melt and become water if the temperature is raised". Thus temperature change involves a phase transition and consequently the latent heat of fusion. This continual phase transition ties the latent heat of fusion inseparably with the specific heat, so much so that the conventional description of the specific heat must be abandoned.

The "specific heat" that will be used in the rest of this paper will mean the 'effective' specific heat of saline ice, which reflects, in addition to the specific heat of its components, the heat of phase transition associated with a temperature change.

1.2 - Historical discussion

Peterson (1883) in 1883 was the first investigator to notice the difference in behaviour of the latent heat of fusion of saline ice in comparison with the same property for fresh water ice. He noticed that there was a trend in the results for the upper part of the range (i.e. near the melting point) for a very significant increase in the specific heat. Krummel (1907) suggested that the abnormal results for sea ice could be attributed to the brine contained in the ice.

Malmgren (1927), was to confirm Krummel's hypothesis in the 'Maud' expedition of 1918-1925. Malmgren was the first person to empirically determine the specific heat of sea ice and to point out that the high specific heat of sea ice near the freezing temperature is created by the fact that at temperatures somewhat below the freezing temperatures, even slight increments in the temperature of the sample will cause noticeable changes in the amount of ice per unit volume.

There have been other measurements done on the specific heat of ice, notably Dickinson and Osborne (1915), Maass and Waldbauer (1925), Barnes and Maass (1930), and Nernst, Koref and Lindeman (1910). However it should be noted that all these measurements were made on ice from pure and distilled (sometimes twice distilled) water. All noticed that impurities greatly influence the specific heat of ice, especially near the melting temperatures.

Measuring of the same property for saline ice had largely been neglected since Malmgren's historical determination. In 1957 Nazintsev (1960) reopened the discussion by making several measurements on the drifting station 'North-Pole-4 in the Arctic. Schwerdtfeger (1962) and Ono (1966) have both done largely theoretical work in the determination of the specific heat of ice. Ono has also done some empirical determination of specific heat near the melting point temperatures.

1.3 - Present Study

Thermal properties are functions of salinity and temperature. This work is largely experimental and involves the redetermination of the specific heat of saline ice for a temperature range from -23° celsius to the melting point of ice. This is to be repeated for a range of salinities from 0 (i.e. fresh water ice) to 10 parts per thousand (10°/oo). It is also to check the theoretical work done by Schwerdtfeger in 1962.

Malmgren's determination of the specific heat, although valuable, gives at most a general and approximate idea of the ability of ice to store heat. Since then, measuring the specific heat has largely been neglected; but in the light of the development of the Arctic region it is becoming more and more relevant. Determining the specific heat involves difficult and exacting experiments involving calorimetry. Specific heat values are important and necessary to determine the heat stored in the ice and also in finding the amount of heat transfer through an ice cover. Together with the heat balance equation, the specific heat values will enable one to forecast and compute the growth and the decay of an ice cover.

Diffusivity, $\underline{K}$, varies directly as the thermal conductivity and inversely as the product of the density and the specific heat. It is worth noting that all three are varying (non-linear) functions of salinity and temperature. Thus accurate determination of the specific heat, and consequently diffusivity will enable one to better solve the heat diffusion equation.

$$\frac{\partial T}{\partial t} = \frac{K}{c\rho}\frac{\partial^2 T}{\partial x^2} = \underline{K}\frac{\partial^2 T}{\partial x^2}$$

Where T = temperature

t = time

x = space coordinate

K = thermal conductivity

C = specific heat

ρ = density

$\underline{K}$ = diffusivity

These and many other major problems can be aided in their solution by a better understanding and determination of the specific heat of sea ice.

Chapter 2 - Theoretical Discussion

2.1 - A Model for Sea Ice

In the understanding of the physical properties of sea ice, details about the configuration and the constituents of ice should be known. The model used to describe the thermal properties here is as given by Assur (1958). A piece of sea ice is an immensely complex unit consisting of pure ice platelets, solid salt precipitates, air bubbles and brine pockets.

A sheet of ice normally consists of long and vertical ice crystals. The cross-sectional area of these crystals being several square centimeters. Figure 1, (after Assur) shows such a sea ice crystal made up of pure ice plates in the direction of growth. The direction of the C-axis in neighbouring crystals is perpendicular to G axis, the growth axis, but arbitrary in the B-C plane. This is shown in the figure by the double edged arrows.

The brine cells are usually long with respect to their diameter. Studies indicate that they run through a major portion of the length of an ice sheet. They are not continuous but have occasional vertical interruptions. The amount of brine in the cells depends largely on the temperature. There is also a dependance on the salinity for a given temperature. Figure 2 (after Assur) shows the brine cells as they would appear in normal sea ice. The cells shown have a circular cross-section but in nature they can be flattened cylinders. The brine cells are separated (along the C axis) by plates of pure ice. In a study by Langleben (private communication) the average spacing between the brine columns was found to be about 0.46 mm.

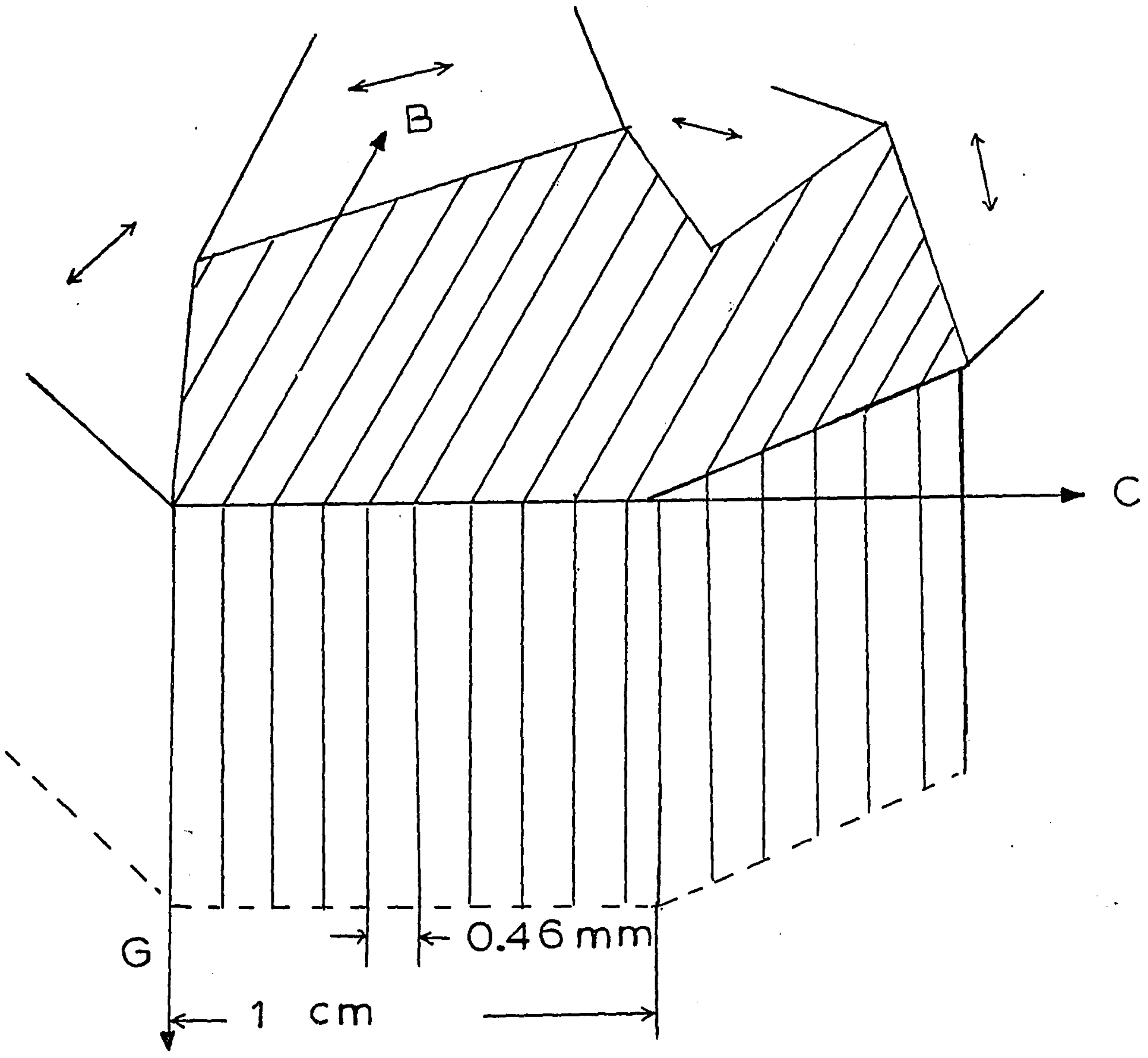


FIGURE 1
MODEL FOR SEA ICE

LINES INDICATE LOCATION OF PLATES WITH BRINE CELLS

C - PRINCIPAL CRYSTALLOGRAPHIC AXIS

B - DIRECTION OF BRINE POCKETS

G - DIRECTION OF GROWTH AND OF BRINE CYLINDERS

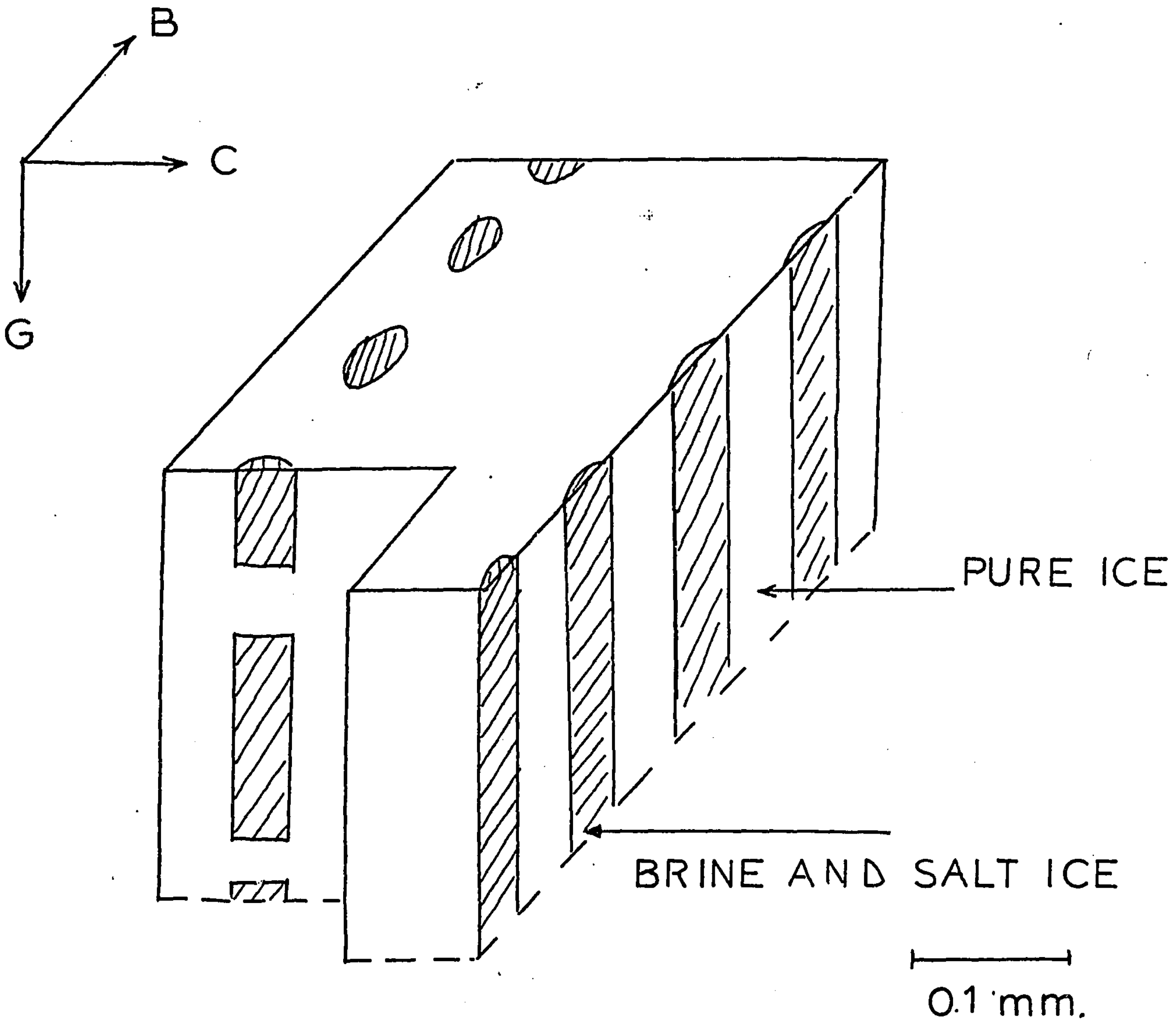


FIGURE 2

CYLINDRICAL SHAPE OF BRINE CELLS

The salinity of the ice is also a function of the freezing rate. As there is little or no substitution for the hydrogen and oxygen atoms in the ice lattice, the salinity of the ice will depend on the amount of brine trapped in the ice. The faster the freezing rate, higher the salinity of the ice will be.

The concentration of the brine in the brine cells is such that it is in thermal equilibrium with the surrounding ice. Thus the salinity and the temperature together with time determine the content of brine in the ice.

As air is dissolved in water there are air bubbles formed in the sea ice when the water freezes. Air, having a low heat capacity with respect to water, would tend to change the heat capacity of a sample of ice. Thus air bubbles also play a part in the properties of ice.

In cooling the sea water below the freezing point, certain salts that make up the brine begin to precipitate as solid salt crystals. Sodium sulphate decahydrate ($Na_2SO_4 \cdot 10\ H_2O$) salts begin precipitating at -8.2°C and go on precipitating in significant amounts till -34°C. At -22.9°C it is the dihydrate of sodium chloride ($NaCl \cdot 2\ H_2O$) that starts precipitating heavily on further cooling. Potassium chloride and magnesium chloride dodecahydrate (KCl and $MgCl_2 \cdot 12\ H_2O$) begin precipitating at -36°C and -42°C respectively. At about -54°C calcium chloride hexahydrate ($CaCl_2 \cdot 6\ H_2O$) begins its precipitation. There is evidence to believe that there is no electrically active liquid brine in the sea ice below -60°C. Addison (private communication) observed identical behaviour in the electrical properties of pure and saline ice from liquid nitrogen temperature to about -60°C. On further heating i.e. above -60°C, there appeared to be a divergence of the dielectric coefficient of saline ice from that of pure water ice.

The phase diagram for sea ice is given in Figure 3, as it appeared in Anderson's paper (Anderson, 1961). The volume phase diagram is important in calculating the density and the latent heat together with the specific heat. The curves show that the composition varies rapidly when the ice is near its melting point and thus great changes in the physical properties would be expected when ice is melting or forming. This can be seen later in the study of specific heat. Changes in salinity also produce noticeable changes in the specific heat, as is seen in the curves for ice of low salinities.

It is however, convenient to consider the phase diagram for sea water where freezing point of the brine is plotted against the mass ratio of the dissolved salts to pure water. Such a plot is found in Nelson and Thompson (1954) and is reproduced as Figure 4.

It has been said that there is a dependance of the physical properties of ice on salinity, temperature and time. The dependance of the properties on salinity and temperature was exhibited above. The time dependance of the properties is on the freezing rate of the ice, on brine drainage and on the migration of brine cells in the ice. It is known that younger ice is more saline than older ice. This is because of the drainage of brine from the ice to the sea. The drainage of the brine is quite rapid near the melting point of ice.

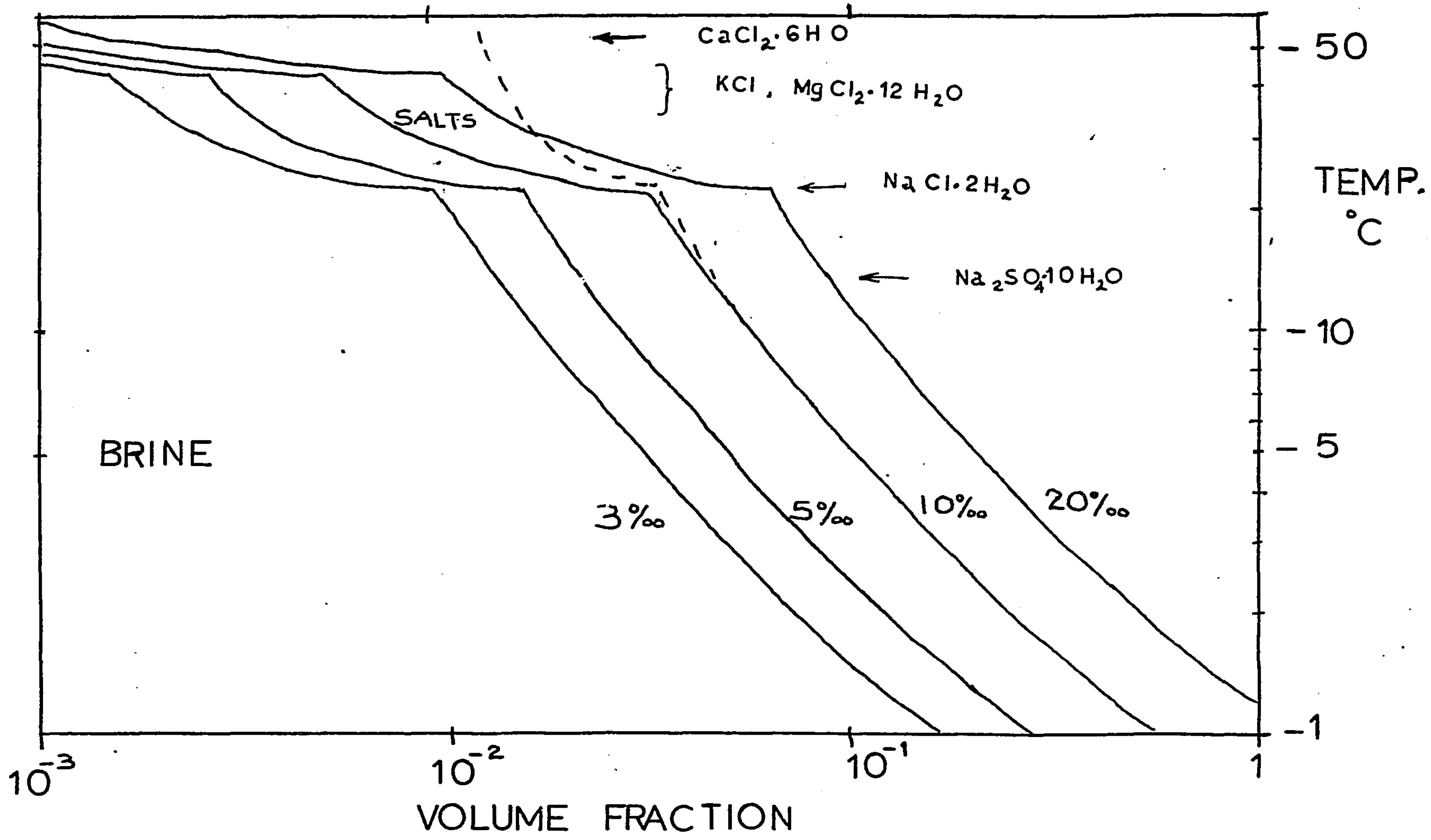


FIGURE 3 VOLUME PHASE RELATION IN SEA ICE FOR SEVERAL SALINITIES

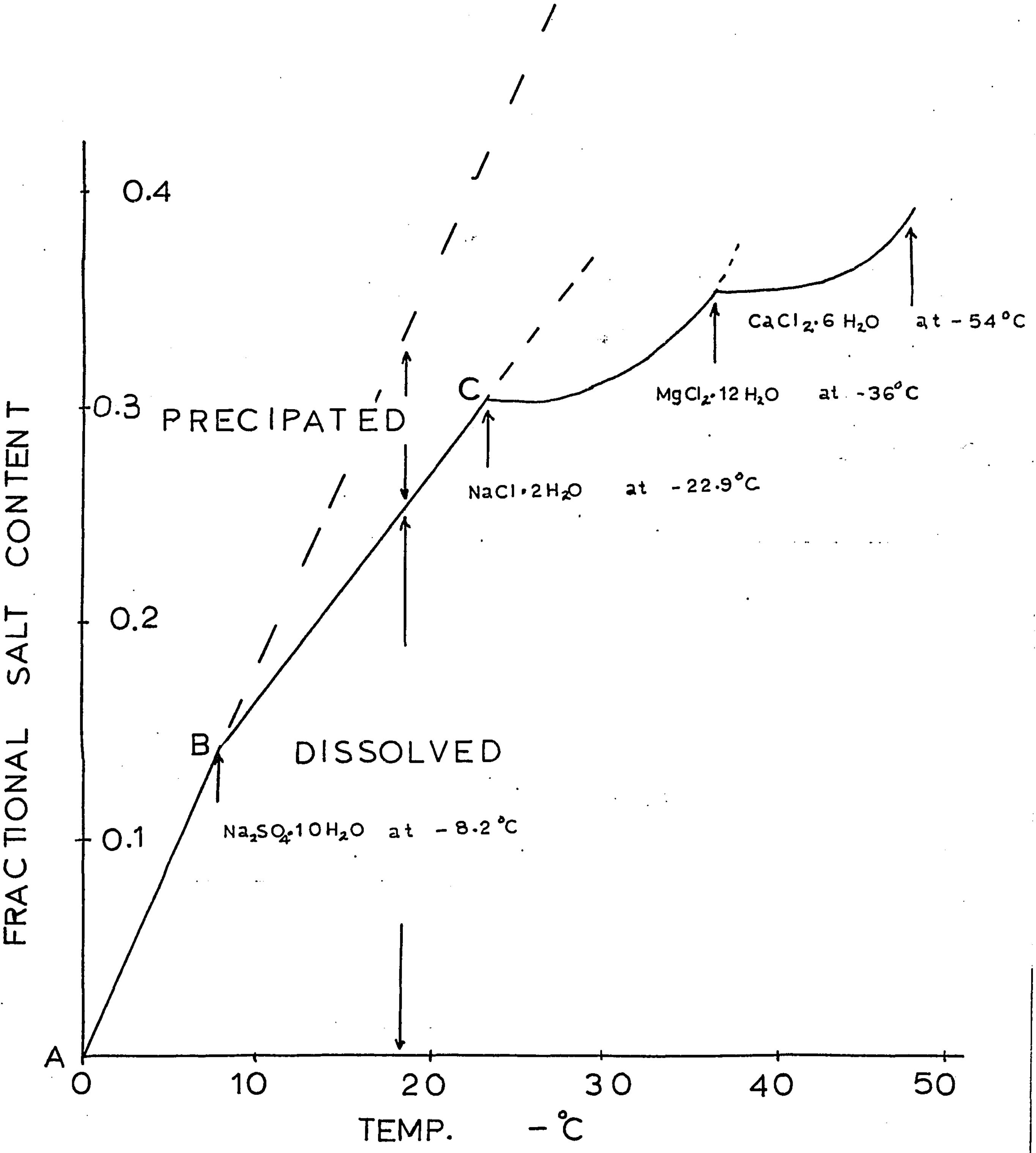
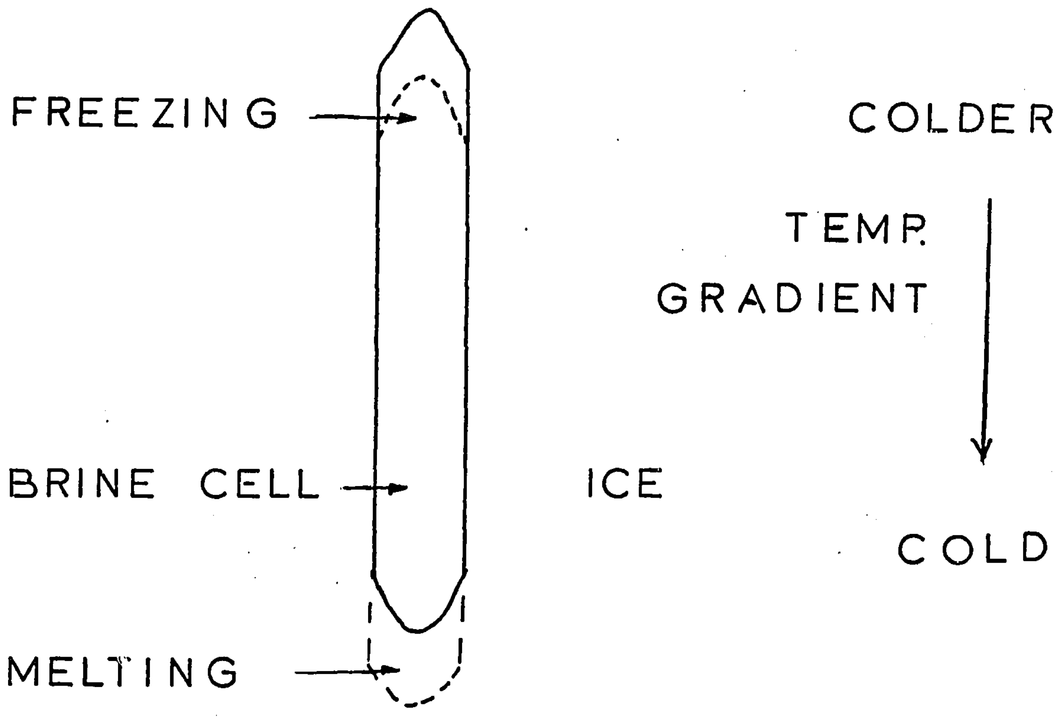


FIGURE 4. PHASE DIAGRAM FOR SEA WATER. FREEZING POINT OF BRINE AS PLOTTED AGAINST THE MASS RATIO OF DISSOLVED SALTS TO PURE WATER.

The phenomenon of brine migration is described in Pounder (1965) and briefly it is as follows. Assume the conditions as shown in Figure 5 below.



MIGRATION OF BRINE CELLS

FIGURE 5

Now because of diffusion, the concentration of brine within the pocket will be uniform, and the salinity comparable with the mean temperature of the ice surrounding the cell. Thus at the warmer end the brine is too concentrated and will dissolve ice to reduce its concentration. At the colder end more ice freezes to increase the brine concentration, and the net effect is that there is a migration of the brine cell along the temperature gradient in the direction of increasing temperature.

2.2 - The Specific Heat of Sea Ice between the Freezing Point and -8.2°C

This study is to check the validity of the derivation of the theoretical relation for the specific heat of ice by Schwerdtfeger (1962). We begin by defining σ as the salinity and S as the fractional salt content of the brine, within the ice which is at temperature T.

If we start out with M grams of sea ice, then that sea ice will contain in it

$$W = \frac{M\sigma}{S} \tag{1}$$

grams of pure water, $M\sigma$ grams of salt and

$$m = M - M\sigma - \frac{M\sigma}{S} \quad \text{grams of pure ice} \tag{2}$$

Changes in temperature will cause changes in the amount of brine, pure ice,etc,present because of the continual phase changing that takes place with any temperature change. The change in the amount of pure water is given by

$$dW = -\frac{\sigma M}{S^2} \quad dS \tag{3}$$

Now according to Figure 4, there is a linear relationship between the fractional salt content and the temperature in this range, and this relation is

$$S = \alpha T \tag{4}$$

S = fractional salt content of brine

T = temperature - deg. celsius

α = the slope of the line AB

$= -0.01848\ {}^{o}C^{-1}$

with this substitution (3) becomes

$$dW = -\frac{\sigma M}{\alpha T^2}\, dT \tag{5}$$

Essentially the specific heat of sea ice depends on the amount of water substance changing state during temperature changes, the specific heats of pure ice and water, the specific heat of the salts and the heat of crystallization. The latter two are neglected since the contribution to the specific heat of the sea ice by the thermal capacity of the dissolved salts is of the order 8×10^{-4} for a salinity of $4\ {}^{o}/_{oo}$. The amount of heat required to dissolve 0.004 gm of Nacl is less than 0.008 calories, according to Lange (1952). Therefore the heat of crystallization can be neglected.

The heat absorbed $\text{đ}Q$ by a mass of sea ice is then taken up in three ways, namely the heat to transform dW grams of ice into water, the heat absorbed by the pure ice to raise its temperature by an increment dT and the heat absorbed by water to raise its temperature dT.

Thus

$$\text{đ}Q = L_i\, dW + \left(M - M\sigma - \frac{M\sigma}{S}\right) C_i\, dT + \left(\frac{M\sigma}{S}\right) C_w\, dT \tag{6}$$

where Li = Latent heat of fusion for pure ice

Ci = Specific heat of pure ice

Cw = Specific heat of pure water

Cp = Specific heat of saline ice at constant pressure

$$Cp = \frac{1}{M} \left.\frac{dQ}{dT}\right|_p$$

thus

$$Cp = -\frac{\alpha Li \sigma}{S^2} + \left(1 - \sigma - \frac{\sigma}{S}\right) Ci + \frac{\sigma}{S} Cw \qquad (7)$$

or

$$Cp = -\frac{\sigma Li}{\alpha T^2} + \frac{\sigma}{\alpha T}(Cw - Ci) + Ci \qquad (8)$$

Where we have used (4) and (5) to simplify (7) and neglected $-\sigma Ci$ since for natural sea ice σ is less than 5 °/oo (5×10^{-3})

Li = 79.69 Cal/gm

Cw = 1.01 Cal/gm°C

Ci = the specific heat of pure ice, which, for a temperature range from -40°C to -0.05°C, to within the limits of experimental error is given by the equation

$Ci = 0.5057 + 0.001863T$

T in degrees celsius

The above relationship between pure ice and temperature was obtained from Dickinson and Osborne (1915). This work is regarded as the most precise work on the specific heat of pure water ice and is thus taken as a value for Ci in this experiment.

2.3 - The Specific Heat of ice between -8.2°C and -23°C.

From Figure 4, we see that there is a continuous deposition of $Na_2SO_4 \cdot 10\ H_2O$ between -8.2°C and -34°C. In this range it is more suitable to consider MS as the amount of salt dissolved, in grams; and Mp as the amount of precipated salts as solid salt crystals. Note, however, that Mp does not include the water of crystallization.

The linear rate of deposition of sodium sulphate decahydrate ($Na_2SO_4 \cdot 10\ H_2O$) in Figure 4 indicates the use of the fractional salt content plot rather than the conventional phase diagram. The amount of precipitate can easily be calculated by noting the difference between the actual and the projected value on the phase diagram. The extrapolated line indicates the salinity of the brine as it would have been had no crystallization taken place and the solid line is the salinity with the precipitation as in the real case. Thus reiterating, there are MS grams of dissolved salts and Mp grams of precipitated salts in M grams of sea ice. There is also βWp grams of water involved in the crystallization of the salts. β for $Na_2SO_4 \cdot 10\ H_2O$ is 1.27
Then the mass of pure water is

$$W = \frac{M\sigma}{S+p} \tag{9}$$

and that of pure ice is

$$m = M - M\sigma - \frac{M\sigma}{S+p} - \frac{M\sigma\beta p}{S+p} \tag{10}$$

Where the last two terms are due to the water in the brine and water in the crystal. $M\sigma$ is the amount of salt present.

The change in the mass of pure water for a change in salinity dS and the associated precipitated dp in a temperature change dT is

$$dW = -\frac{\sigma M}{(S+p)^2}\,(dS + dp) \tag{11}$$

with the aid of Figure 4 we get the relationship between S and p as

$$S = \alpha T - p \tag{12}$$

and

$$p = \alpha'\,(T + 8.2) \tag{13}$$

for the temperature range of $-8.2^{\circ}C$ to $-23^{\circ}C$.

α' = slope of the line BC

= $-1.0308 \times 10^{-2}\ {}^{\circ}C^{-1}$

Thus (11) takes the form

$$dW = -\frac{M\sigma}{\alpha T^2}\,dT \tag{14}$$

The heat supplied, $đQ$, is absorbed in the same way as before, as well as by the water trapped in the crystallization of Na_2SO_4 and by the thermal capacity of the solid sodium sulphate.

Thus

$$đQ = L_i\,dW + \left\{M - M\sigma - \frac{M\sigma}{S+p}\left(1+\beta p\right)\right\} C_i\,dT + \left(\frac{M\sigma}{S+p}\right) C_w\,dT + \left(\frac{M\sigma}{S+p}\right)\left(1+\beta\right) p\,C_h\,dT \tag{15}$$

Ch - the specific heat of the hydrated sodium sulphate.

The last term is the direct contribution to the specific heat by the heat capacity of $Na_2SO_4 \cdot 10H_2O$

or

$$C_p = \frac{1}{M}\left.\frac{đQ}{dT}\right|_p = -\frac{\sigma L_i}{\alpha T^2} + \left\{1 - \sigma - \frac{\sigma}{S+p}\left(1+\beta p\right)\right\} C_i + \frac{\sigma}{S+p} C_w + \left(\frac{\sigma}{S+p}\right) p\left(1+\beta\right) C_h \tag{16}$$

which, upon the use of (13) yields

$$Cp = -\frac{\sigma}{\alpha T^2} L_i + (1-\sigma) C_i + \frac{\sigma}{\alpha T} (C_w - C_i)$$
$$+ \sigma \left(\frac{\alpha'}{\alpha}\right) \left(\frac{T + 8.2}{T}\right) \left\{ (1+\beta) C_h - \beta C_i \right\} \qquad (17)$$

The two terms in the curly brackets are both of order one.

$$\frac{\alpha'}{\alpha} \approx 1$$

and

$$\frac{T + 8.2}{T} \approx 1$$

Thus together with the fact that $\sigma \sim 10^{-3}$ we can neglect the last term and drop $-\sigma C_i$ from the second term in the right hand side of (17). Thus

$$Cp = -\frac{\sigma}{\alpha T^2} L_i + \frac{\sigma}{\alpha T} (C_w - C_i) + C_i \qquad (18)$$

is the relationship for the specific heat of saline ice for the temperature range from -23°C to the melting point of ice.

2.4 - Theoretical Results

The values for the specific heat of saline ice as determined from (18) are given below, in Table 1 and Figure 6. Similar calculations of equations (8) and (18) can be found in Schwerdtfeger (1962).

Table 1

Temp. °C	Specific Heat of Saline Ice Cal/gm°C		
	Salinities		
	0°/oo	2°/oo	4°/oo
-23.0	0.4629	0.4808	0.4988
-22.0	0.4647	0.4843	0.5039
-21.0	0.4666	0.4880	0.5094
-20.0	0.4684	0.4920	0.5155
-19.0	0.4703	0.4963	0.5224
-18.0	0.4722	0.5011	0.5300
-17.0	0.4740	0.5063	0.5386
-16.0	0.4759	0.5122	0.5486
-15.0	0.4778	0.5190	0.5602
-14.0	0.4796	0.5268	0.5739
-13.0	0.4815	0.5360	0.5904
-12.0	0.4833	0.5470	0.6107
-11.0	0.4852	0.5607	0.6361
-10.0	0.4871	0.5780	0.6689
- 9.0	0.4889	0.6007	0.7125
- 8.0	0.4908	0.6316	0.7724
- 7.0	0.4927	0.6757	0.8587
- 6.0	0.4945	0.7424	0.9903
- 5.0	0.4964	0.8515	1.2066
- 4.0	0.4982	1.0501	1.6020
- 3.0	0.5001	1.4758	2.4514
- 2.0	0.5020	2.6846	4.8672
- 1.0	0.5038	9.1821	17.8603

Table 1A

Temp.	Specific Heat of Saline Ice		Cal/gm°C
°C	Salinities		
	6°/oo	8°/oo	10°/oo
-23.0	0.5167	0.5347	0.5526
-22.0	0.5234	0.5430	0.5626
-21.0	0.5308	0.5523	0.5737
-20.0	0.5391	0.5627	0.5862
-19.0	0.5484	0.5744	0.6004
-18.0	0.5589	0.5878	0.6167
-17.0	0.5709	0.6033	0.6356
-16.0	0.5849	0.6213	0.6576
-15.0	0.6014	0.6426	0.6838
-14.0	0.6210	0.6682	0.7153
-13.0	0.6449	0.6994	0.7538
-12.0	0.6744	0.7380	0.8017
-11.0	0.7116	0.7871	0.8626
-10.0	0.7599	0.8508	0.9417
- 9.0	0.8242	0.9360	1.0477
- 8.0	0.9132	1.0540	1.1948
- 7.0	1.0417	1.2247	1.4078
- 6.0	1.2382	1.4860	1.7339
- 5.0	1.5617	1.9168	2.2719
- 4.0	2.1539	2.7058	3.2576
- 3.0	3.4271	4.4028	5.3784
- 2.0	7.0498	9.2324	11.4150
- 1.0	26.5385	35.2167	43.8950

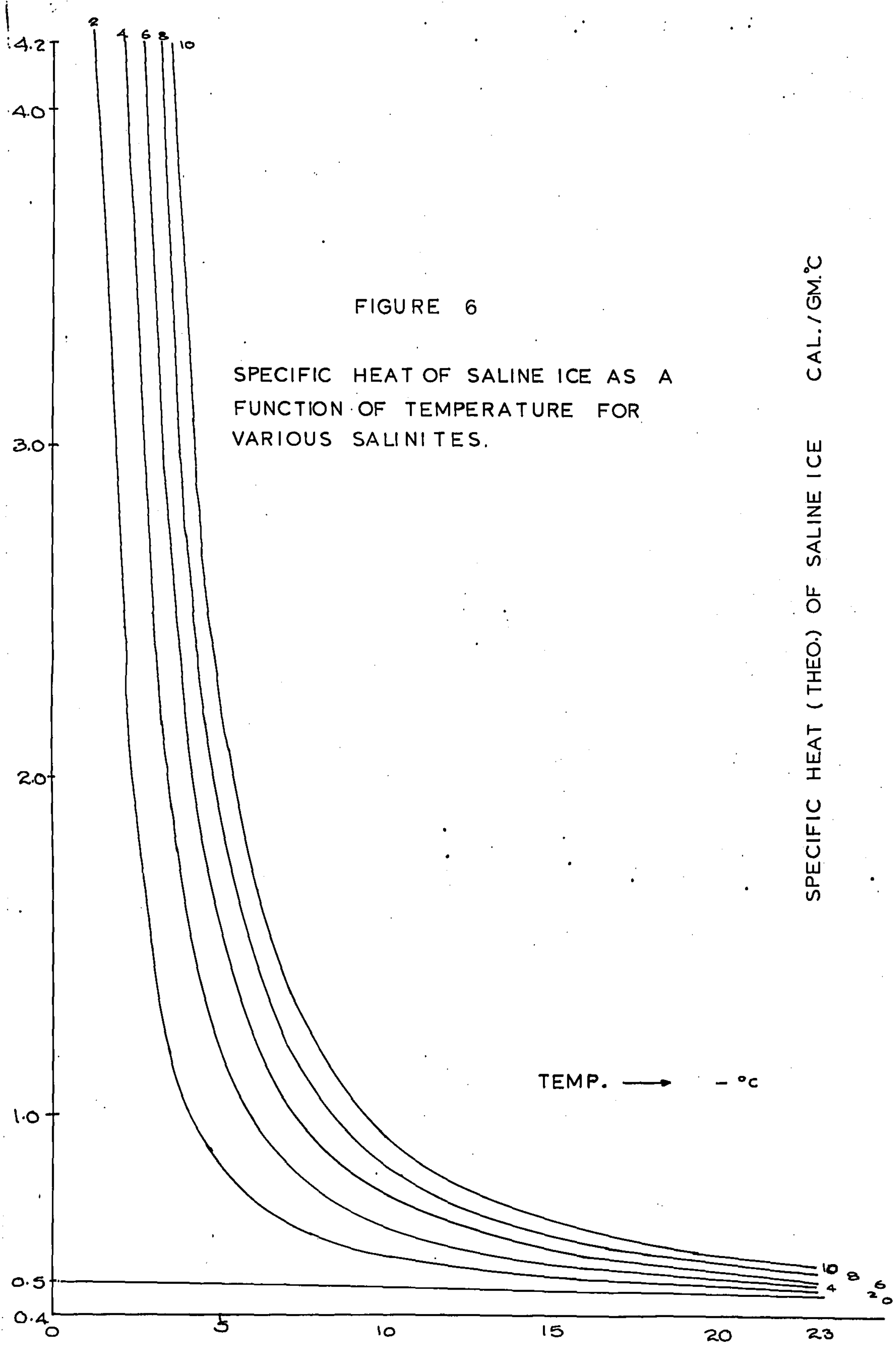


FIGURE 6

SPECIFIC HEAT OF SALINE ICE AS A FUNCTION OF TEMPERATURE FOR VARIOUS SALINITES.

Chapter 3 - Experimental Technique

The experiment performed to determine the specific heat of saline ice was one of calorimetry. The experiment consisted of heating carefully measured amounts of n-heptane and saline ice in a dewar. The initial and final temperatures, together with the energy supplied, were recorded and the specific heat was calculated, as described later on in the chapter.

A brief description of certain aspects of the experiment precedes the actual experimental technique. This is done to show why the experiment was performed the way it was.

Sea ice in a large block, initially at a constant temperature throughout, will develop a temperature gradient (spacially) upon heating. This temperature gradient will eventually disappear as the block attains thermal equilibrium again, but during this time heat can escape from the calorimeter and the resulting calculations of the specific heat might be inaccurate. To eliminate the temperature gradient that might develop in a large block of ice, the ice used in the experiment was crushed into small pieces of no more than 1 - 2 cm^3. Thus when the ice is heated and the gradient does develop, it quickly disappears as the whole piece soon comes to a constant temperature.

The calorimetric fluid used in the experiment was n-heptane. Normal heptane was chosen because it is a pure hydrocarbon that does not dissolve any ice nor any of the salts that are present in sea ice. The complete immiscibility of heptane and ice together with the fact that it does not have any phase transition in the temperature range -90°C to +90°C makes n-heptane an ideal medium to conduct heat, and produce uniform temperature distributions in the calorimeter. Further information on n-heptane is given in Appendix 1.

The amount of heptane and ice used in each run was carefully measured in a Mettler balance and placed in a dewar. The mixture of heptane and ice (about 300 grams of each) was then gently stirred. The heat supplied, and the temperature changes were measured by the probe as depicted in Figure 7. Figure 8 shows how the probe fits into the dewar.

The probe was constructed out of glass tube, to hinder thermal conduction by the probe, with the conducting wires to the heater running through the tube. The heater was made from 30 gauge iron wire wound so as to produce a noninductive resistance of 23 Ω. The thermocouples used to measure the temperature are located as shown in Figure 7. The thermocouple closest to the heater is designated by T and the one farther away by T' Two thermocouples are used so as to determine when thermal equilibrium is reached. As a check, a third thermocouple was set up in a differential manner to measure the differences in temperature between regions close to the heater and regions far from the heater in the heptane - ice mixture. Thus when this Δ T thermocouple read $0\,\mu v$ (or $\pm 2\,\mu v$ i.e. $\pm 4/100^{\circ}C$) thermal equilibrium was assumed.

The thermocouples used were those made out of iron and constantan wires. They were calibrated and this is elaborated upon in Appendix 2.

The dewar, after being sealed by the probe, was placed in a jacket of styrofoam. This was done, again in an endeavour to diminish the amount of heat escaping from the dewar. Finally the box with the dewar was enclosed in a "cardboard cold room". The cold room, where the experiment was performed, is maintained at $-23^{\circ}C \pm 1^{\circ}C$. (except during the defrost period when the temperature rises to $-16^{\circ}C$). This is much colder than the inside of the dewar (especially towards the end of a run) and thus heat can escape.

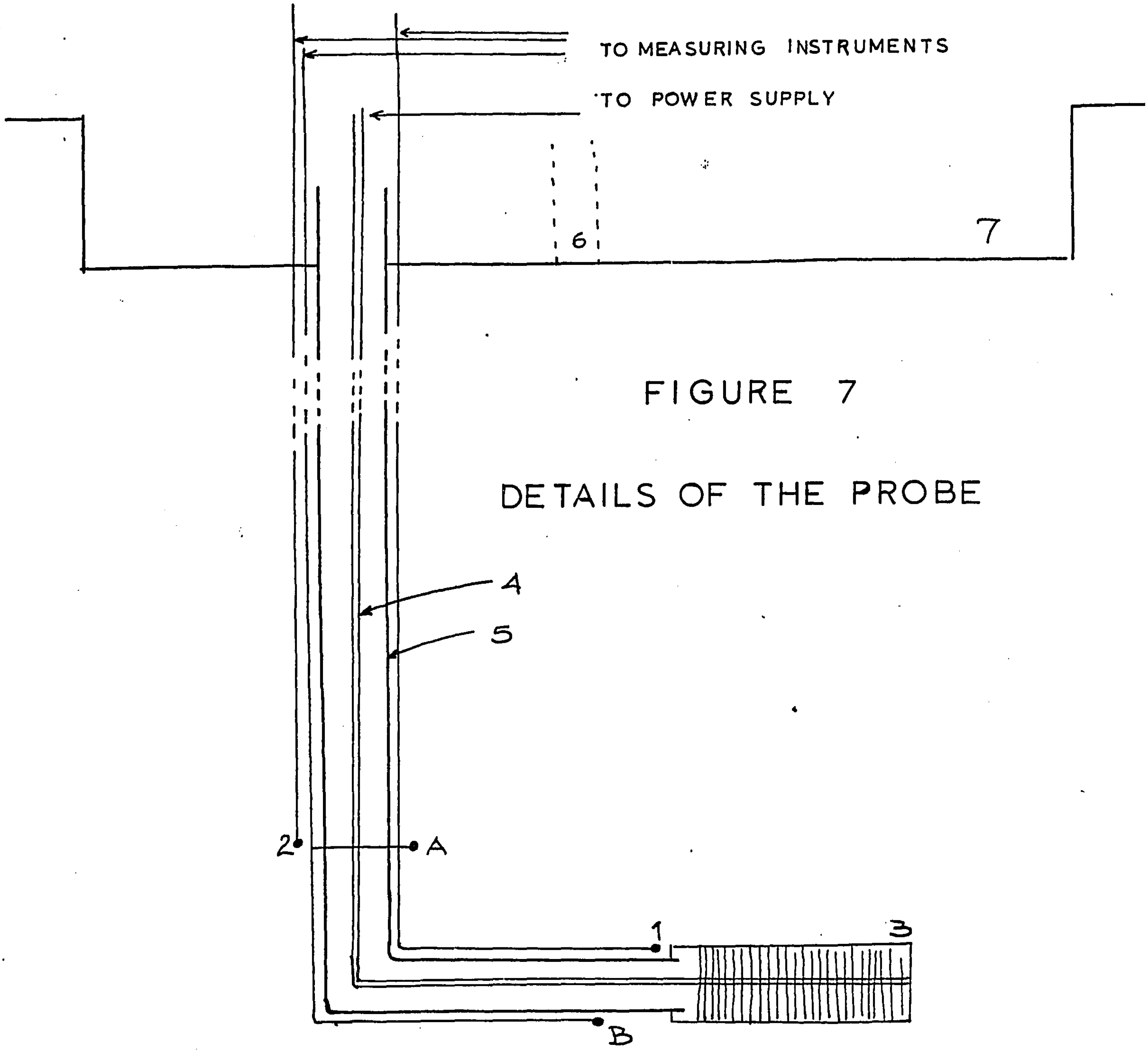
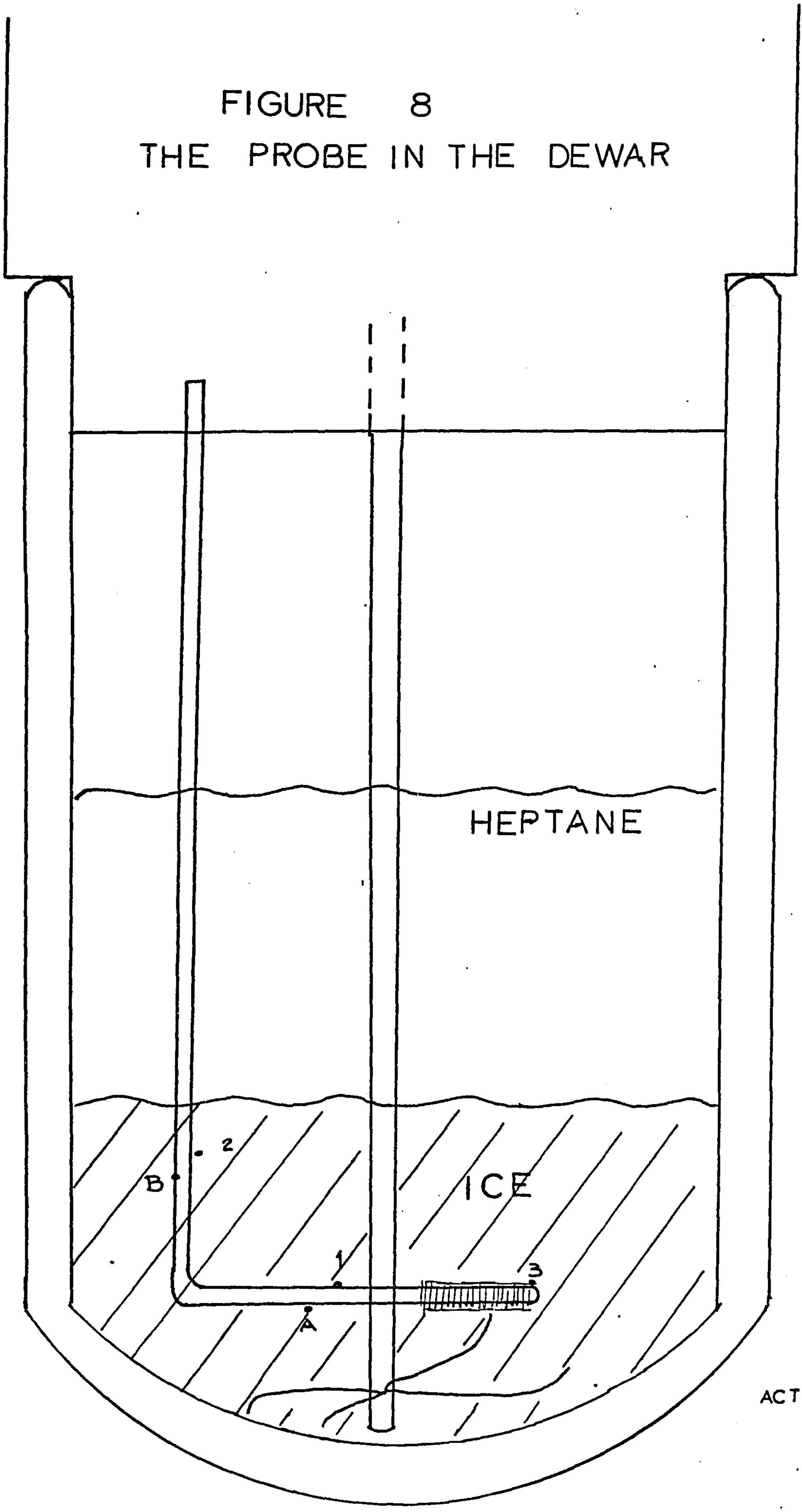


FIGURE 7

DETAILS OF THE PROBE

FIGURE 8
THE PROBE IN THE DEWAR



ACTUAL SIZE

To minimize this, the auxiliary cold room was created. The purpose of this was to keep the temperature, both inside and outside the dewar, the same. This was accomplished by simultaneously heating the sample and the 'cardboard cold room' by independent power supplies. The temperature of the auxiliary cold room was recorded and adjusted to match the temperature inside the dewar. A schematic sketch of the apparatus inside the cold room is depicted in Figure 9.

The ice used in the experiment was made by adding salts to distilled water. A measured amount of salt was added to a measured amount of distilled water and then thoroughly mixed. This saline water was then very slowly heated and boiled to expel any dissolved gasses. Any deficiency in the amount of water (due to evaporation) was made up and then the whole volume was frozen. After freezing, the ice was left alone for a few days so that the whole block was at a uniform temperature. The top portion of the block of saline ice was discarded because there was a thick brine sludge on top, due to the rejection of brine by the ice. Only the middle part of the ice block was used which was then crushed into tiny chips of no more than 1-2 cm^3. The amount needed for the experiment was carefully measured and used immediately. A sample of this crushed ice was extracted to determine the salinity of the ice used.

The salts added to the pure water to make saline ice are given in Pounder (1965) and the list is reproduced in Appendix 3. The procedure used to determine the salinity is also given there.

9.

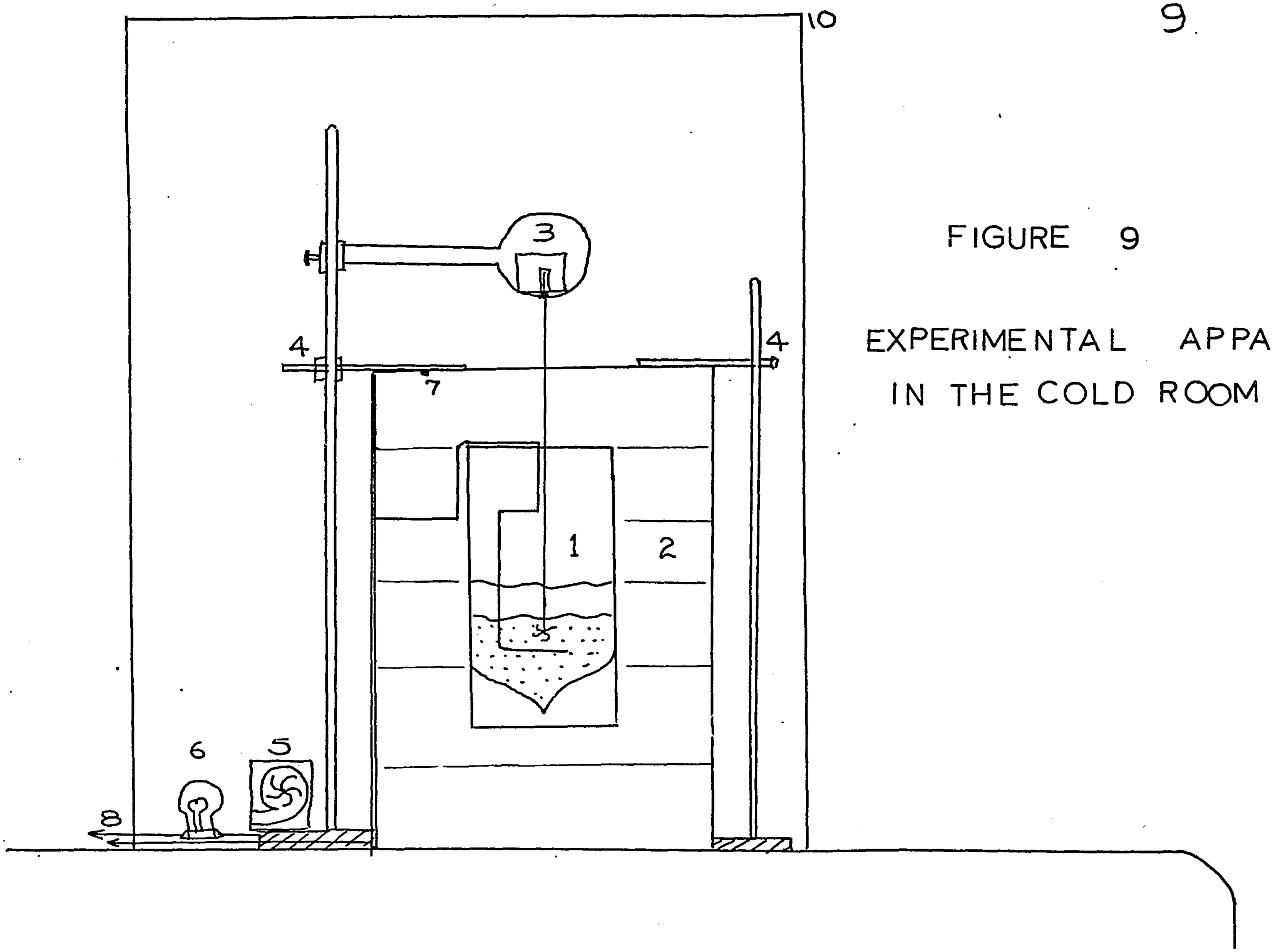


FIGURE 9

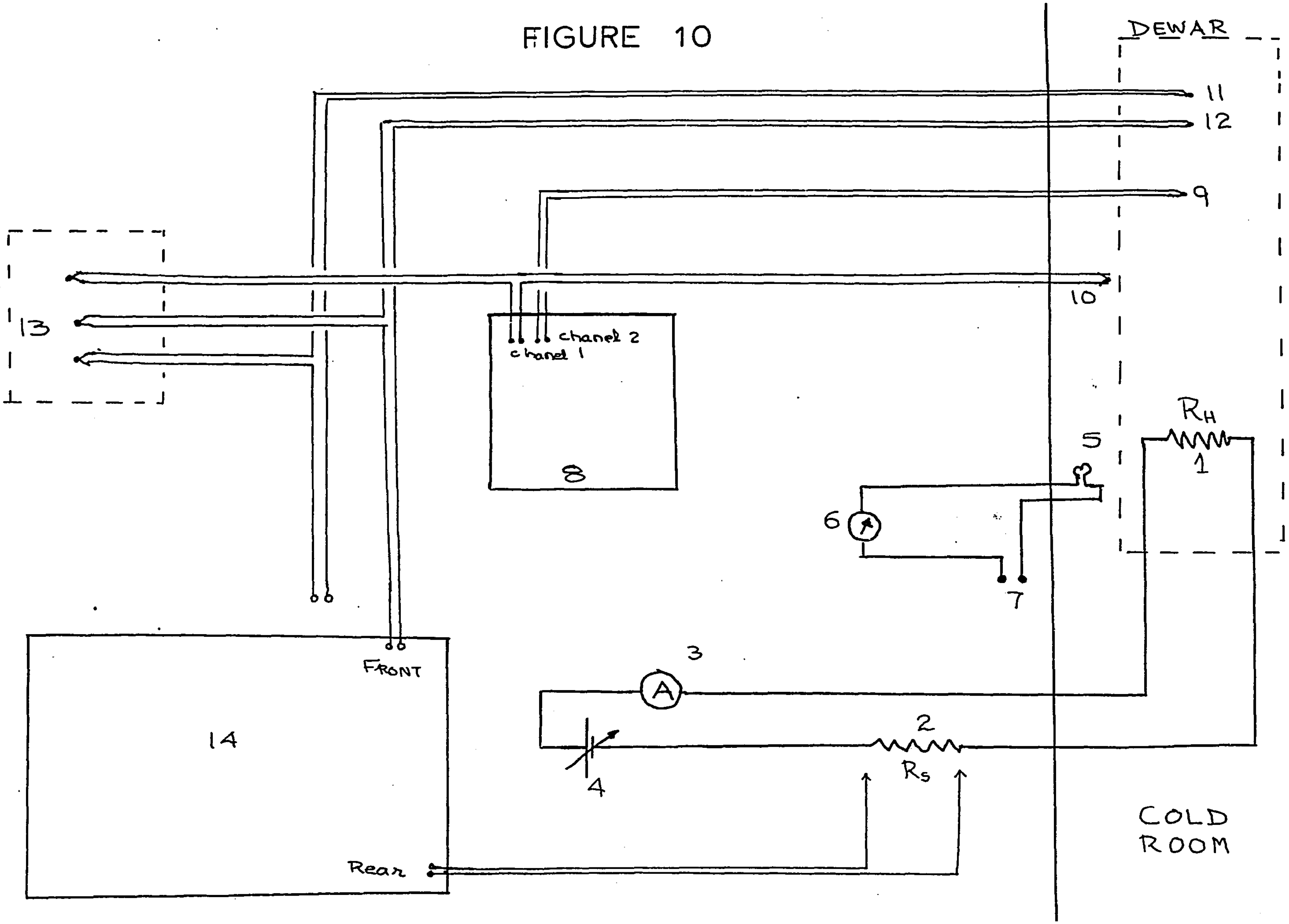
EXPERIMENTAL APPARATUS
IN THE COLD ROOM

The conducting wires from the power supply to the heater were copper. Copper wire is a good means by which heat can be accidentally brought from the control room to the dewar. To stop this a length of this wire was looped inside the 'cardboard cold room' so that all the conducted heat is dissipated outside the dewar and not in it.

The devices used for measuring consist of a Leeds and Northrup differential potentiometer No. 7564 and a Honeywell 2-channel chart recorder 'Electronik 19'. The rest of the equipment used in controlling the experiment is diagramatically shown in Figure 10. The specifications and the inaccuracies in the measurement by the L + N differential potentiometer and the Honeywell recorder are given in Appendix 4.

The experimental procedure was as follows. After the measured amounts (300 grams of each) of heptane and ice was placed in the dewar, the dewar was tightly closed by the probe (and the styrofoam cap). The initial temperature was taken when the ΔT thermocouple showed a reading of zero. After that the heating was started. Heat was supplied by means of a heater built in the probe. The power for the heater was from a Heathkit regulated power supply model IP-20. The current and the voltage across the heater was monitored by the differential potentiometer. After a prescribed period of time (10 minutes in most runs) the power was shut off and one waited for thermal equilibrium to develop (usually in 3 to 5 minutes). When the ΔT thermocouple read $\pm 2 \mu v$ (indicating thermal equilibrium) the final temperature was recorded. During the run, temperatures T and T' were constantly watched for any discrepancies. The size of the temperature step varied from one experiment to the next. There

FIGURE 10


DEWAR
11
12
9
10
13
chanel 2
chanel 1
8
5
R_H
1
6
7
3
A
2
R_s
4
FRONT
14
Rear
COLD ROOM

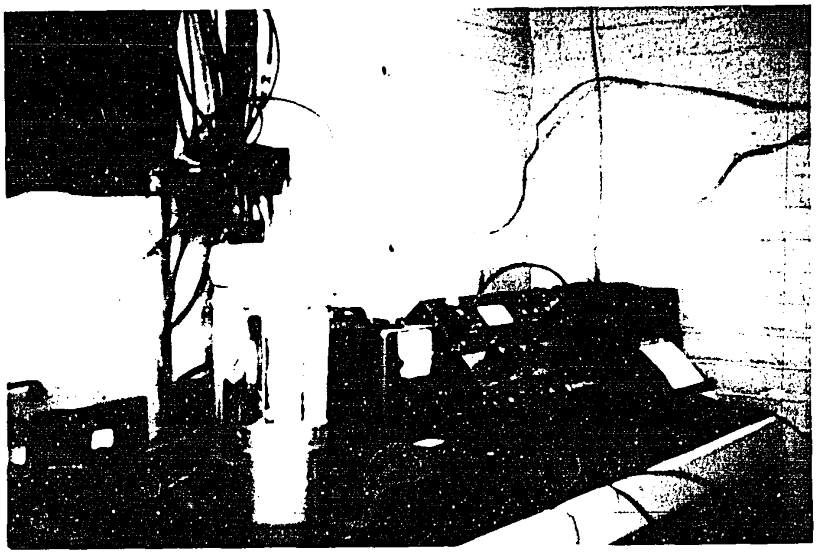


FIGURE 11 POWER SUPPLY AND ICE BATH

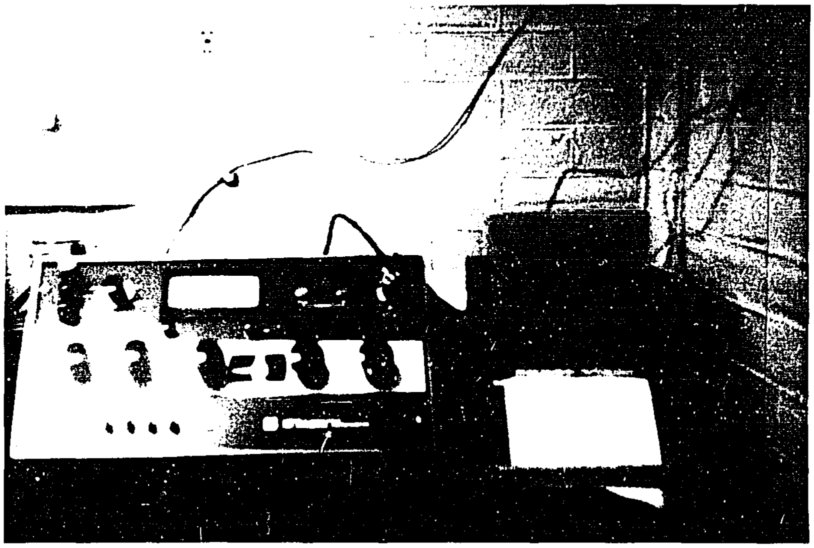


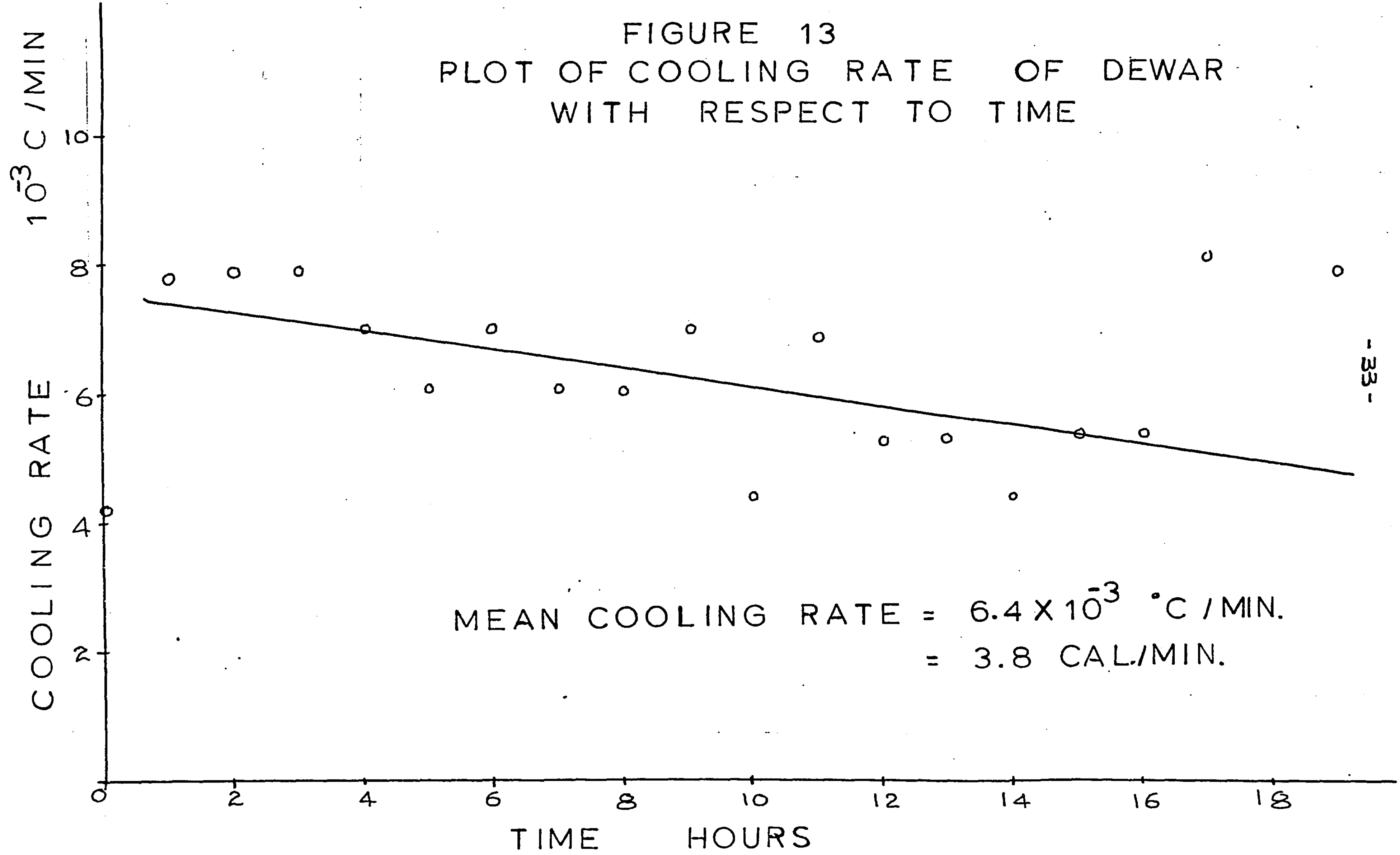
FIGURE 12 MEASURING INSTRUMENTS

was also a variation in the temperature steps within a run. The steps of the temperature was made as small as possible. In the beginning of the experimental run (i.e. towards the -23°C end) the increment of the temperature was of the order of 1.4C° and towards the end (i.e. near the melting point of ice) it was about 0.3C°. The above procedure was repeated till the ice melted. The experiment was reperformed for all salinities (i.e. 0, 2, 4, 6, 8 and 10°/oo) and each salinity was the object of two different runs.

Before the actual calculations of the specific heat could begin the thermal capacity of the dewar,together with the probe, had to be determined. This was obtained in the same way as the procedure described above except that the ice was left out. Since the thermal capacity of the heptane can easily be obtained (with the aid of Table 8 in Appendix 1) the thermal capacity of the calorimeter was obtained.

Even with the delicate mechanism used to minimize the heat losses from the dewar to the cold room, some heat did leave the dewar and some got in from the control room by means of the conducting wires and thermocouples. Thus there was a need for a cooling plot of the dewar. Heptane at an elevated temperature (0°C) was put in the dewar and the rate of decrease of the heptane temperature with time was recorded for a period of time. The cooling rate for the experiment is attached as Figure 13. The average rate of cooling was taken to be 3.84 calories per minute. The cooling rate, together with the heat capacity of the dewar are essential components in the formulae for obtaining the specific heat. To prevent redundancy, the relationship used to calculate the specific heat of ice is not shown here but is shown in Appendix 4.

FIGURE 13
PLOT OF COOLING RATE OF DEWAR
WITH RESPECT TO TIME



MEAN COOLING RATE = 6.4×10^{-3} °C /MIN.
= 3.8 CAL./MIN.

The average possible error with measurements of the experiment was about 2.4%. The possible error in the specific heat of 4°/oo saline ice at -4.5°C was 1.87%. This was typical of the inaccuracies encountered in the experiment. On the warmer part (i.e. near 0°C) the possible error increased as indicated by 5.9% error in the specific heat value at -0.9°C for 8°/oo ice. The highest possible error in the measurement was 11.7% (near the melting temperatures). The higher errors were largely because of the smaller temperature differences encountered at melting point temperatures. A more complete error analysis is in Appendix 4. The inaccuracy in making temperature measurements was a key factor in using this method for experimenting. The method of mixtures involves three distinct temperature measurements whereas the above methods need two. As was shown above, the errors in measuring temperatures can lead to larger errors in determining the specific heat. The results of this experiment are in the next Chapter.

Chapter 4 - Experimental Results

The results of the experiments described above are given in Table 2 - 7 and are plotted as Figures 14 - 19. These results are for salinities ranging from 0°/oo (pure water ice) to 10°/oo. The upper limit on the salinity was taken as 10°/oo since one does not often encounter sea ice of salinity greater than 10°/oo in nature. The lowest temperature at which the specific heat was calculated was -23.00°C and the warmest was -0.30°C.

For the pure water ice, the experimental values of the specific heat deviated from the theoretical specific heat values. This was true at colder temperatures but was quite pronounced at elevated temperatures. The theoretical values, calculated from Schwerdtfeger's work, (Schwerdtfeger, 1963) of the specific heat, remained constant (with a small temperature correction) at 0.5057 cal/gm°C, right down to the melting point for pure ice. In this experiment, however, the specific heat values climbed up to 2.85 cal/gm°C at -0.30°C. A similar trend was noticed in the work by Dickinson and Osborne (1915). Thus reiterating, the experimental values of the specific heat do not remain constant till the melting point but increase rapidly above -3.00°C. It is possible that this deviation was because of some impurities in the distilled water. In the Dickinson and Osborne experiment, twice distilled water was used and still the increase of the specific heat at temperatures near the melting point was observed. The pure water used in this experiment was once distilled and it is possible that some impurities might have contaminated the water (although precautions were taken to prevent this). The increased specific heat at elevated temperatures confirms the comment made earlier about the effects of impurities on the thermal properties of ice.

In the tabulation of the results for saline ice, results are from several runs. Some runs (namely, one for 4°/oo and another for 10°/oo) resulted in completely erroneous values for the specific heat. The faulty values were not included in the results listed here. The runs were discarded because they were performed in the developmental stage of the apparatus. One run on 10°/oo ice had to be aborted because of the failure of the heater in the middle of a run.

There were some results for temperatures near the melting point that also had to be discarded. This was done because the temperature readings were not consistent. The reliability of the temperatures became questionable because of the instability of the readings. The ΔT thermocouple started recording large differences in temperatures at the end of a heating trial and considerable time had to be spent waiting for equilibrium to approach. Even when the ΔT thermocouple read $\pm 2 \mu v$, further fluctuations in the T and T' readings were noticed. This generally occurred for salinities greater than 4°/oo and for temperatures above $-1.00^\circ C$. The fluctuations of the temperatures together with the growing possible error (because of the inaccuracies of the measuring instruments) in the specific heat of ice, lead to the abandoning of these values.

In the data presented here, there is a deviation of the experimental results from the theoretical values. The largest deviation was 21.8% (not counting the ones for fresh water ice near the melting point). For most of the values the % deviation falls within the experimental uncertainties of the calculated values.

TABLE 2

Salinity = $0^{o}/oo$

Temperature °C	Cp exp. cal/gm°c	possible error ± %	Cp theo. Cal/gm°C	% deviation
-23.00	0.5012	1.7	0.4629	8.3
-21.75	0.5051	1.5	0.4652	8.6
-20.79	0.0576	1.2	0.4670	8.7
-19.79	0.4990	1.9	0.4688	6.4
-17.84	0.4984	2.9	0.4725	5.5
-16.88	0.5081	4.5	0.4743	7.1
-16.71	0.4558	3.3	0.4746	4.0
-14.96	0.5253	2.2	0.4778	9.9
-14.08	0.4507	2.4	0.4795	6.0
-13.32	0.4760	2.6	0.4809	1.0
-12.67	0.4626	2.2	0.4821	4.0
-12.48	0.5082	2.8	0.4824	5.3
-10.82	0.4856	2.5	0.4855	0.0
-10.81	0.5105	2.3	0.4856	5.1
-10.01	0.4731	2.5	0.4871	2.9
-9.05	0.4856	3.7	0.4888	0.7
-7.90	0.5299	2.4	0.4910	7.9
-7.39	0.5104	2.7	0.4919	3.8
-7.30	0.4769	2.1	0.4921	3.1
-7.05	0.5104	2.1	0.4926	3.6
-6.93	0.5099	1.9	0.4928	3.5
-6.37	0.5041	2.2	0.4938	2.1

TABLE 2 - cont.

Salinity = $0^{o}/oo$

Temperature °C	Cp exp. Cal/gm°C	possible error ± %	Cp theo Cal/gm°C	% deviation
-5.77	0.4938	4.3	0.4950	0.2
-4.45	0.5003	3.8	0.4974	0.6
-3.93	0.5168	3.1	0.4984	3.7
-3.42	0.5321	2.6	0.4993	6.6
-2.99	0.5629	3.4	0.5001	12.6
-2.17	0.5823	5.3	0.5017	16.1
-1.72	0.5983	5.9	0.5025	19.1
-1.28	0.6516	8.5	0.5033	29.5
-0.92	0.7215	6.3	0.5040	43.2
-0.57	1.1876	8.0	0.5046	135.2
-0.30	2.8488	8.9	0.5051	462.0

TABLE 3

Salinity = $2^{o}/oo$

Temperature °C	Cp. exp. Cal/gm°C	possible error ±%	Cp theo. Cal/gm°C	% deviation
-21.82	0.5118	8.0	0.4849	5.5
-19.90	0.5022	6.0	0.4924	2.0
-19.53	0.4903	4.2	0.4940	0.7
-18.45	0.5178	3.7	0.4989	3.8
-17.80	0.5011	3.1	0.5021	0.2
-17.49	0.5034	2.9	0.5037	0.1
-16.56	0.5046	2.7	0.5088	0.8
-16.24	0.5064	2.5	0.5108	0.9
-14.77	0.5278	2.3	0.5207	1.4
-14.50	0.5136	3.1	0.5227	1.7
-13.91	0.5197	4.5	0.5275	1.5
-12.97	0.5296	3.9	0.5363	1.2
-12.46	0.5495	1.7	0.5417	1.4
-11.65	0.5529	1.7	0.5515	0.3
-11.15	0.5618	1.2	0.5584	0.6
-10.10	0.5696	1.6	0.5761	1.1
-9.78	0.5832	1.7	0.5825	0.1
-9.54	0.5487	3.3	0.5876	6.6
-8.25	0.6290	2.3	0.6229	1.0
-8.01	0.6248	3.3	0.6312	1.0
-7.99	0.6273	3.1	0.6320	0.7
-7.35	0.6600	4.0	0.6583	0.3

Table 3 - Cont.

Salinity = $2^{o}/oo$

Temperature °C	Cp. exp. Cal/gm°C	possible error ±%	Cp theo. Cal/gm°C	% deviation
-6.81	0.6824	3.9	0.6862	0.6
-5.46	0.7813	4.0	0.7940	1.6
-5.02	0.8500	1.7	0.8487	0.2
-4.20	1.0138	1.9	0.9990	1.5
-4.03	1.1123	1.7	1.0420	6.7
-3.14	1.4547	2.1	1.3912	4.6
-3.09	1.4784	1.7	1.4201	4.1
-2.31	2.3537	2.0	2.1405	10.0
-1.90	2.6893	2.7	2.9191	7.9
-1.61	3.5437	4.5	3.8630	8.3
-1.22	5.0047	7.9	6.3418	21.1
-1.03	7.0692	10.9	8.6854	18.6
-0.95	11.4078	4.6	10.1168	12.8
-0.71	21.4207	11.8	17.6890	21.1
-0.60	25.6898	10.0	24.5515	4.6

TABLE 4

Salinity = 4°/oo

Temperature °C	Cp. exp. Cal/gm°C	possible error ± %	Cp theo. Cal/gm°C	% deviation
-21.30	0.5365	4.0	0.5077	5.7
-20.86	0.5167	5.4	0.5102	1.3
-19.07	0.5364	3.4	0.5218	2.8
-17.44	0.5296	3.0	0.5347	1.0
-17.25	0.5518	2.6	0.5364	2.9
-16.47	0.5646	2.0	0.5437	3.8
-15.54	0.5679	2.9	0.5537	2.6
-13.76	0.5712	2.5	0.5776	1.1
-13.57	0.5861	3.2	0.5806	0.9
-12.14	0.6125	1.8	0.6076	0.8
-11.99	0.6200	2.6	0.6109	1.5
-10.50	0.6610	2.7	0.6514	1.5
-10.30	0.6695	2.7	0.6582	1.7
-8.65	0.7253	1.3	0.7312	0.8
-7.22	0.7995	2.7	0.8367	4.4
-6.91	0.8771	1.6	0.8683	1.0
-5.61	1.1055	1.7	1.0612	4.2
-4.54	1.3618	1.9	1.3566	0.4
-4.40	1.2997	1.6	1.4117	7.9
-3.40	1.9727	1.6	2.0220	2.4
-2.64	3.0327	1.9	3.0154	0.6
-2.12	4.2804	2.3	4.3895	2.5

TABLE 4 - cont.

Salinity = 40/oo

Temperature °C	Cp exp. Cal/gm°C	possible error ±%	Cp theo. Cal/gm°C	% deviation
-1.81	5.7489	5.5	5.8261	1.3
-1.52	6.8018	5.4	8.0388	15.4
-1.17	15.1519	3.1	13.1958	14.8
-1.03	18.1042	7.6	16.8669	7.3

TABLE 5

Salinity = 6%

Temperature °C	Cp exp. Cal/gm°C	possible error ±%	Cp theo. Cal/gm°C	% deviation
-21.53	0.5336	2.5	0.5268	1.3
-21.08	0.5377	3.5	0.5302	1.4
-20.66	0.5515	3.1	0.5336	3.4
-19.81	0.5497	2.9	0.5408	1.6
-19.01	0.5652	2.9	0.5483	3.1
-18.75	0.5520	2.7	0.5509	0.2
-18.15	0.5738	2.3	0.5572	3.0
-17.63	0.5786	2.6	0.5632	2.7
-16.52	0.5918	1.9	0.5774	2.5
-15.71	0.6020	2.0	0.5894	2.1
-15.39	0.6105	1.5	0.5946	2.7
-14.38	0.6183	1.0	0.6131	0.8
-14.03	0.6243	1.1	0.6204	0.6
-13.24	0.6289	1.1	0.6387	1.5
-12.42	0.6555	1.3	0.6612	0.9
-12.31	0.6758	1.9	0.6645	1.7
-11.30	0.7135	1.8	0.6995	2.0
-10.84	0.7234	1.8	0.7185	0.7
-10.06	0.7429	1.8	0.7566	1.8
- 9.35	0.7893	2.6	0.7994	1.3
- 8.40	0.8658	1.8	0.8739	0.9
- 7.54	0.9483	1.8	0.9661	1.8

TABLE 5 - cont.

Salinity = 6°/oo

Temperature °C	Cp exp. Cal/gm°C	possible error ±%	Cp theo. Cal/gm°C	% deviation
-6.84	0.9982	1.7	1.0709	6.8
-6.60	1.1137	2.5	1.1098	0.3
-5.72	1.2697	2.5	1.3121	3.2
-5.46	1.3262	1.7	1.3910	4.7
-4.99	1.5196	2.0	1.5659	3.0
-4.82	1.5869	2.8	1.6420	3.4
-4.22	2.0569	3.0	1.9871	3.5
-3.70	2.3685	2.5	2.4306	2.6
-3.09	3.4074	2.8	3.2603	4.5
-2.79	3.8981	3.1	3.8807	0.4
-2.10	6.6379	4.2	6.4443	3.0
-1.86	8.4320	3.8	8.0666	4.5
-1.48	15.1366	3.6	12.4233	21.8
-1.07	26.7508	5.1	23.2531	15.0

TABLE 6

Salinity = 8°/oo

Temperature °C	Cp exp. Cal/gm°C	possible error ±%	Cp theo. Cal/gm°C	% deviation
-20.93	0.5750	2.4	0.5530	4.0
-20.06	0.5683	4.1	0.5620	1.1
-19.47	0.5740	2.9	0.5687	0.9
-18.39	0.5816	4.0	0.5824	0.1
-18.07	0.6038	3.4	0.5868	2.9
-16.70	0.6052	2.6	0.6084	0.5
-16.52	0.6173	2.7	0.6116	0.9
-15.38	0.6407	3.0	0.6341	1.0
-14.94	0.6527	2.3	0.6440	1.3
-14.11	0.6594	2.6	0.6651	0.9
-13.28	0.6960	2.7	0.6900	0.9
-11.67	0.7649	2.4	0.7529	1.6
-10.11	0.8500	2.3	0.8429	0.8
-8.60	1.0000	2.1	0.9784	2.2
-7.18	1.0830	1.9	1.1888	8.9
-5.86	1.4613	1.8	1.5335	4.7
-4.67	1.9844	1.7	2.1224	6.5
-4.58	2.1653	1.9	2.1863	1.0
-3.63	3.0152	1.7	3.1739	5.0
-2.94	4.1238	1.7	4.5624	9.6
-2.26	7.3785	2.1	7.3491	0.4

TABLE 6 - cont.

Salinity = $8^{o}/oo$

Temperature °C	Cp exp. Cal/gm°C	possible error ±%	Cp theo. Cal/gm°C	% deviation
-2.07	8.6590	2.2	8.6551	0.0
-1.57	13.9854	3.4	14.6342	4.4
-1.10	29.5804	4.7	29.2094	1.3
-0.86	55.3097	5.9	47.3986	16.7

TABLE 7

Salinity = 10°/oo

Temperature °C	Cp exp. Cal/gm°C	possible error ±%	Cp theo. Cal/gm°C	relative error I%
-20.89	0.5850	2.5	0.5750	1.7
-19.73	0.6134	3.0	0.5899	4.0
-18.62	0.6270	2.8	0.6063	3.4
-17.54	0.6284	3.0	0.6250	0.5
-16.49	0.6648	2.9	0.6464	2.9
-15.44	0.6754	2.3	0.6717	0.5
-14.41	0.7130	2.1	0.7017	1.6
-13.38	0.7462	2.1	0.7382	1.1
-12.40	0.7809	1.9	0.7812	0.0
-11.49	0.8524	1.6	0.8308	2.6
-10.57	0.8875	1.3	0.8939	0.7
- 9.67	1.0108	1.2	0.9732	3.9
- 8.78	1.0641	1.1	1.0759	1.1
- 7.94	1.1851	1.3	1.2054	1.7
- 7.15	1.3533	1.1	1.3701	1.2
- 6.43	1.5874	1.2	1.5752	0.8
- 5.82	1.8363	1.9	1.8109	1.4
- 5.20	1.9966	1.7	2.1393	6.7
- 4.60	2.5377	2.0	2.5904	2.0
- 4.06	3.2615	1.5	3.1774	2.6

TABLE 7 - cont.

Salinity = 10o/oo

Temperature °C	Cp exp. Cal/gm°C	possible error ± %	Cp theo. Cal/gm°C	relative error I%
- 3.60	3.9626	1.7	3.8981	1.7
- 3.21	4.7927	2.0	4.7657	0.6
- 2.87	5.9437	2.4	5.8267	2.0
- 2.60	6.9764	2.9	6.9808	0.1
- 1.98	10.9304	2.8	11.6353	6.1
- 1.73	16.0693	3.6	15.0644	6.7
- 1.62	18.5703	3.5	17.0984	8.6
- 1.31	28.8674	3.1	25.8356	11.7
- 1.10	40.0706	3.2	36.3859	10.1

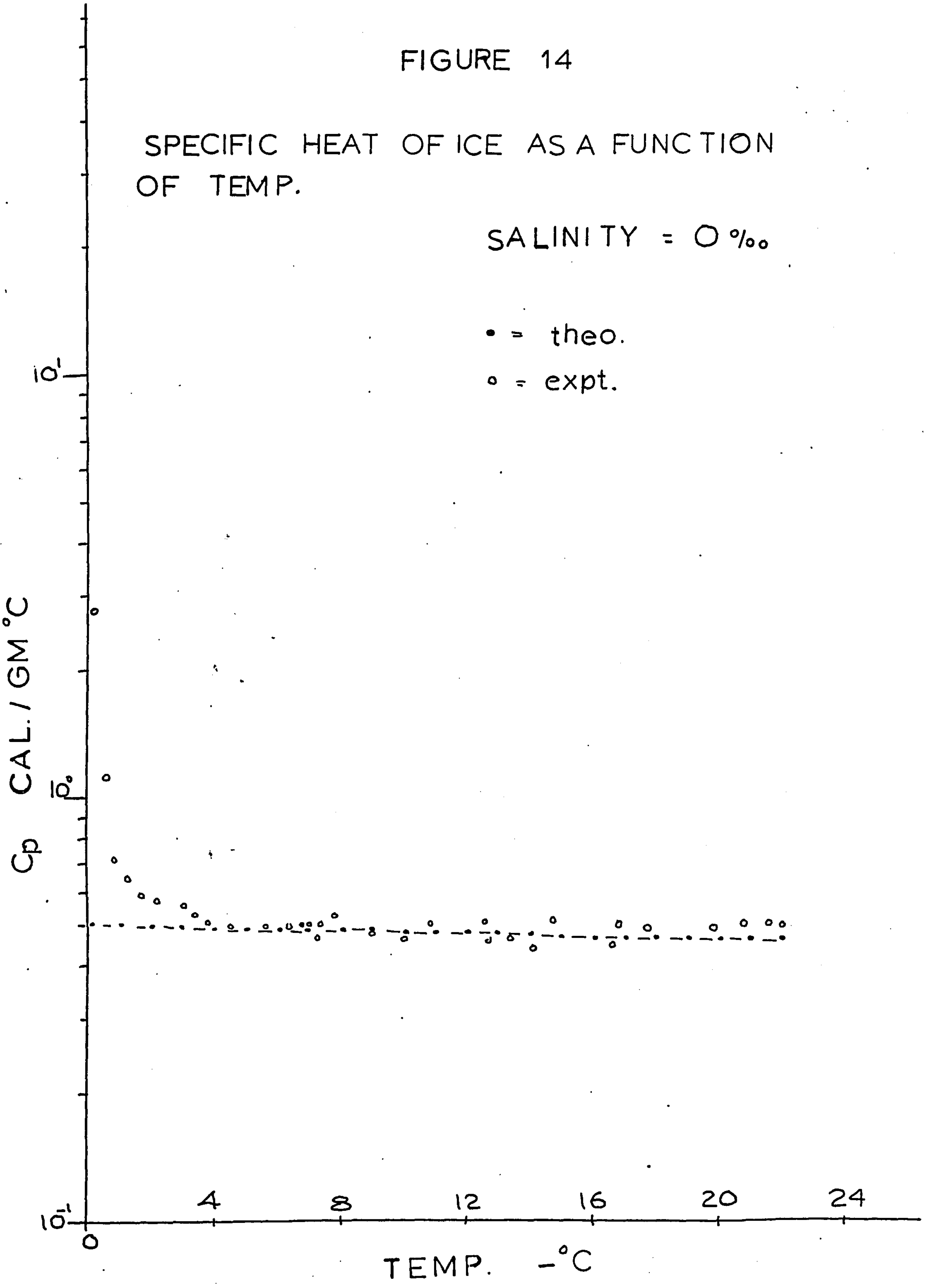


FIGURE 14

SPECIFIC HEAT OF ICE AS A FUNCTION OF TEMP.

SALINITY = 0 ‰

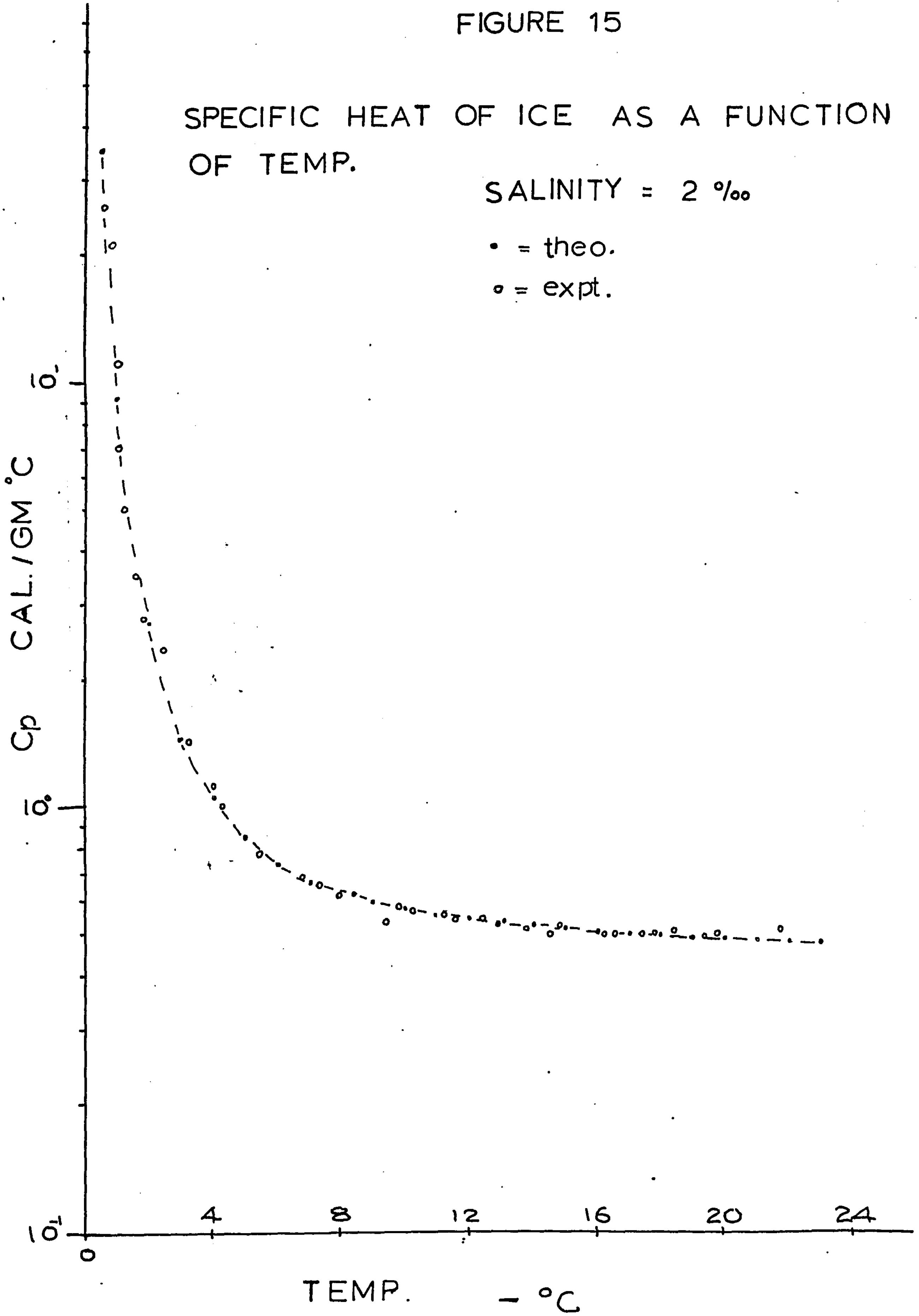


FIGURE 15

SPECIFIC HEAT OF ICE AS A FUNCTION OF TEMP.

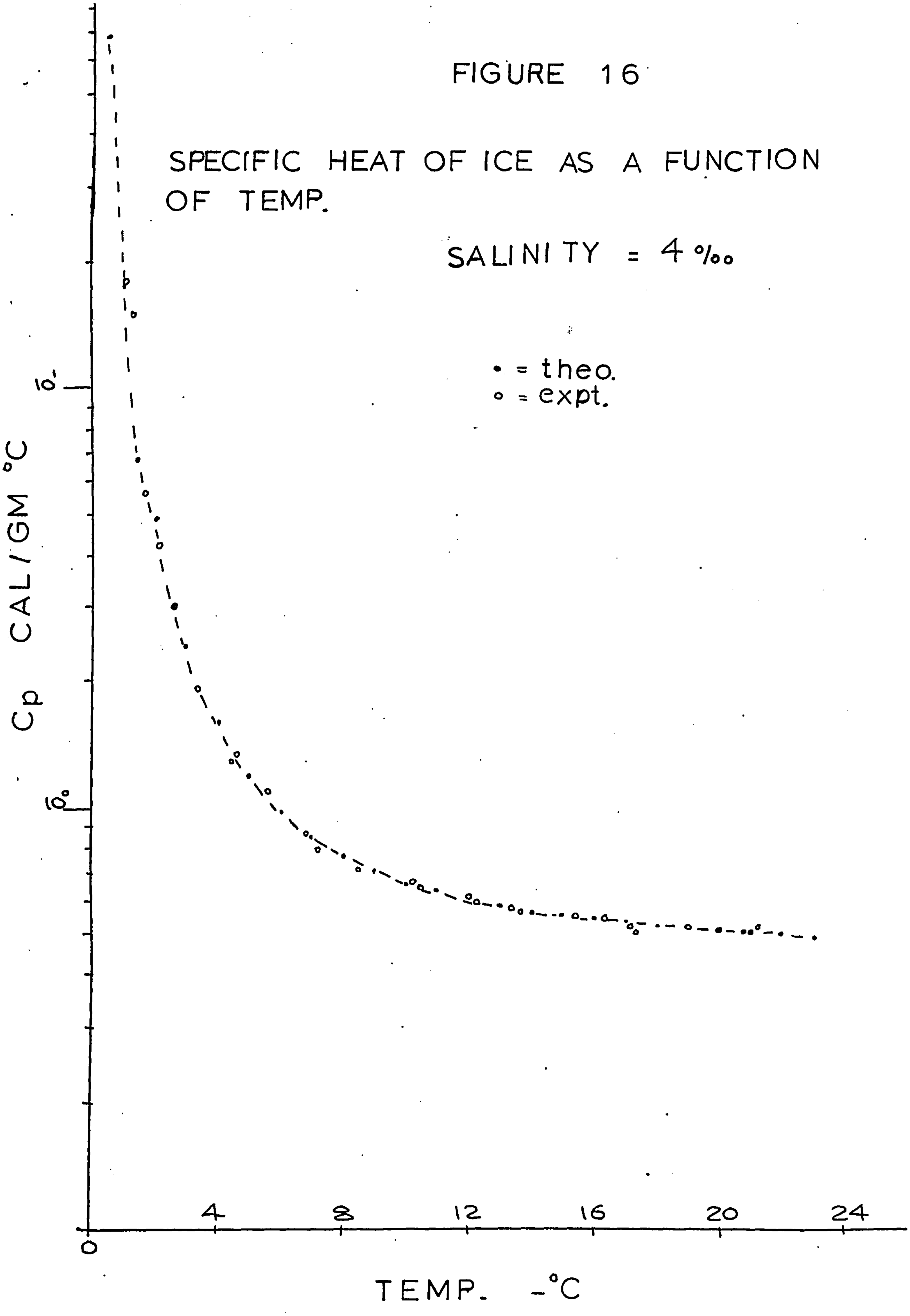


FIGURE 16

SPECIFIC HEAT OF ICE AS A FUNCTION OF TEMP.

SALINITY = 4 ‰

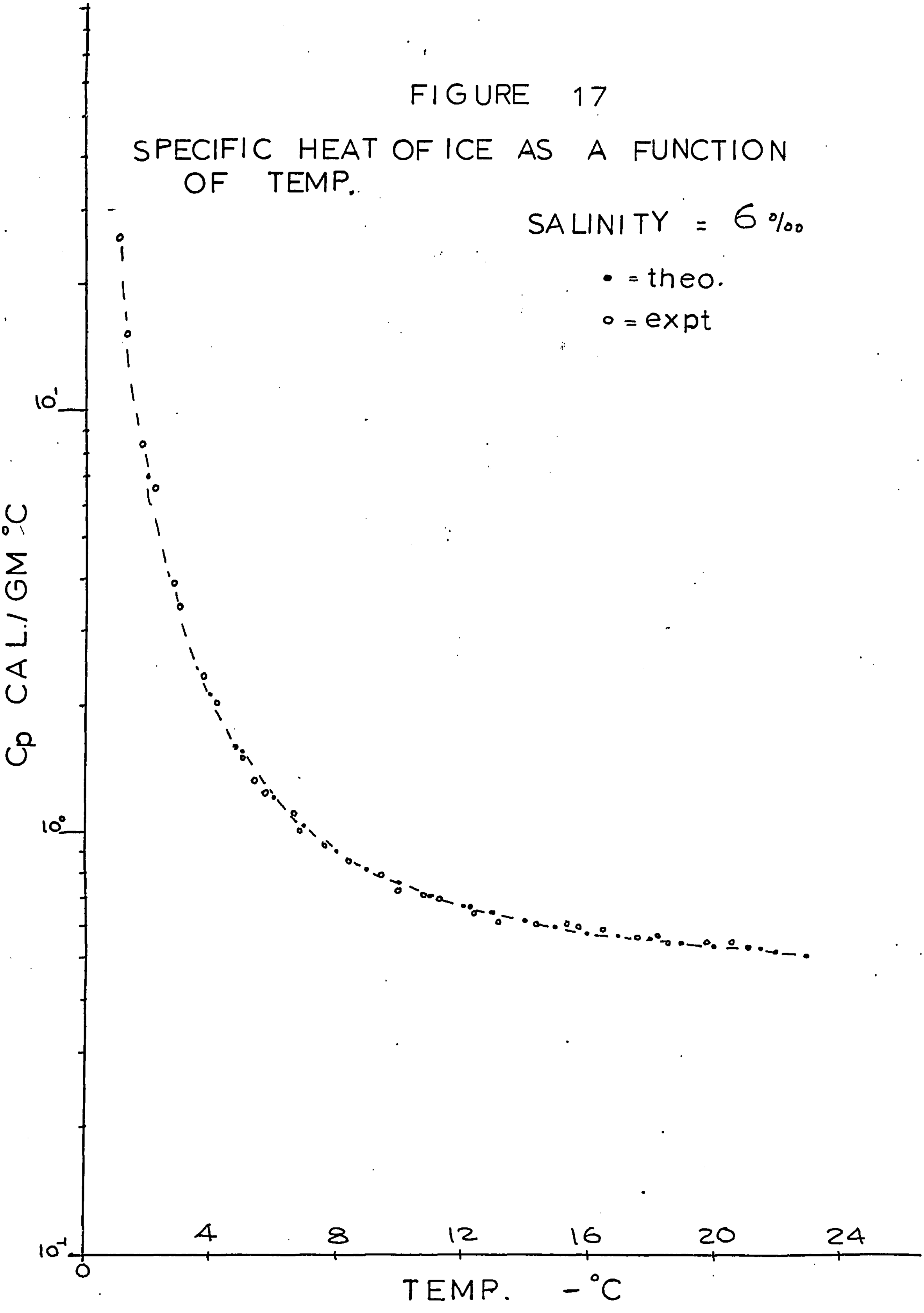


FIGURE 17

SPECIFIC HEAT OF ICE AS A FUNCTION OF TEMP.

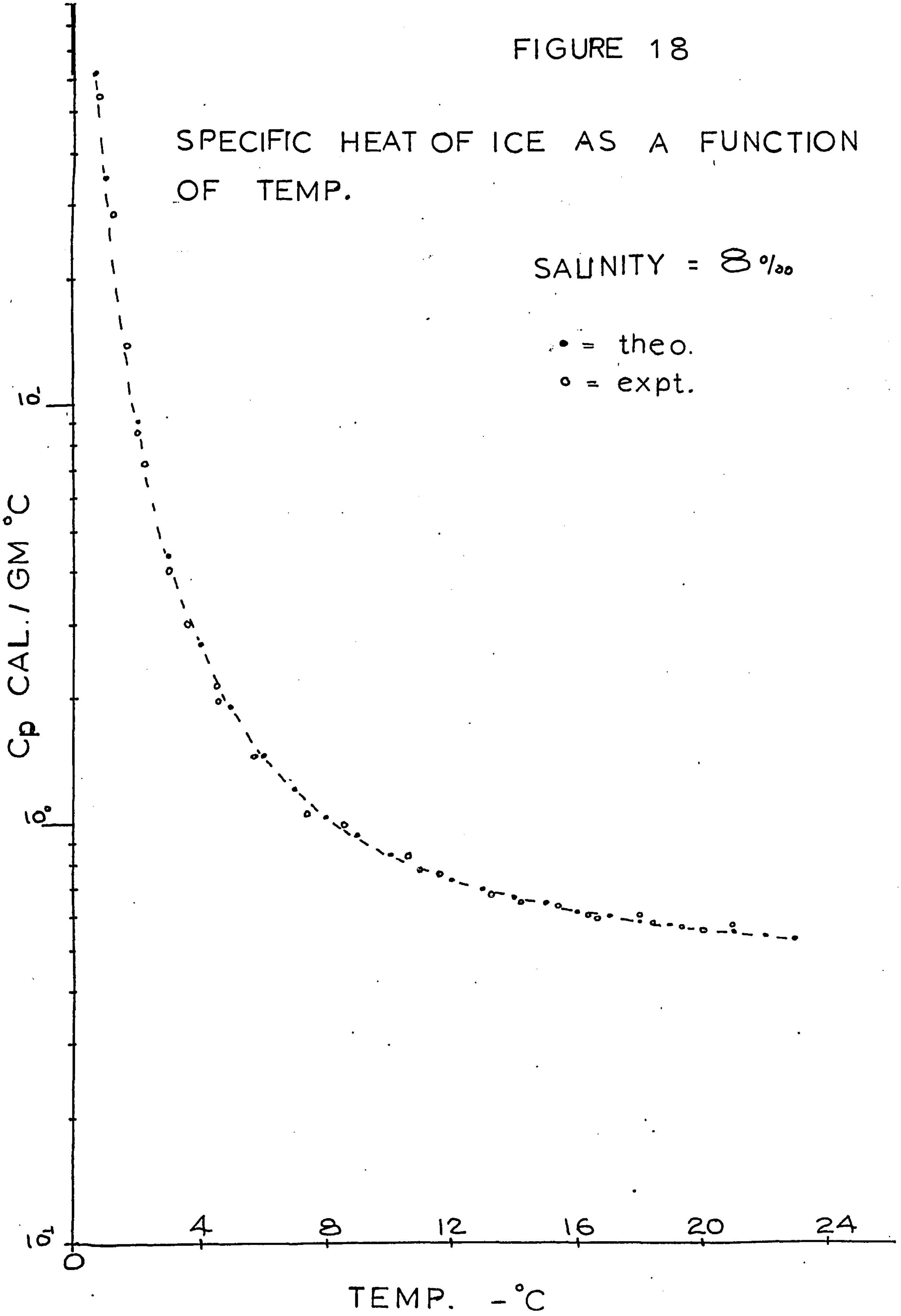


FIGURE 18

SPECIFIC HEAT OF ICE AS A FUNCTION OF TEMP.

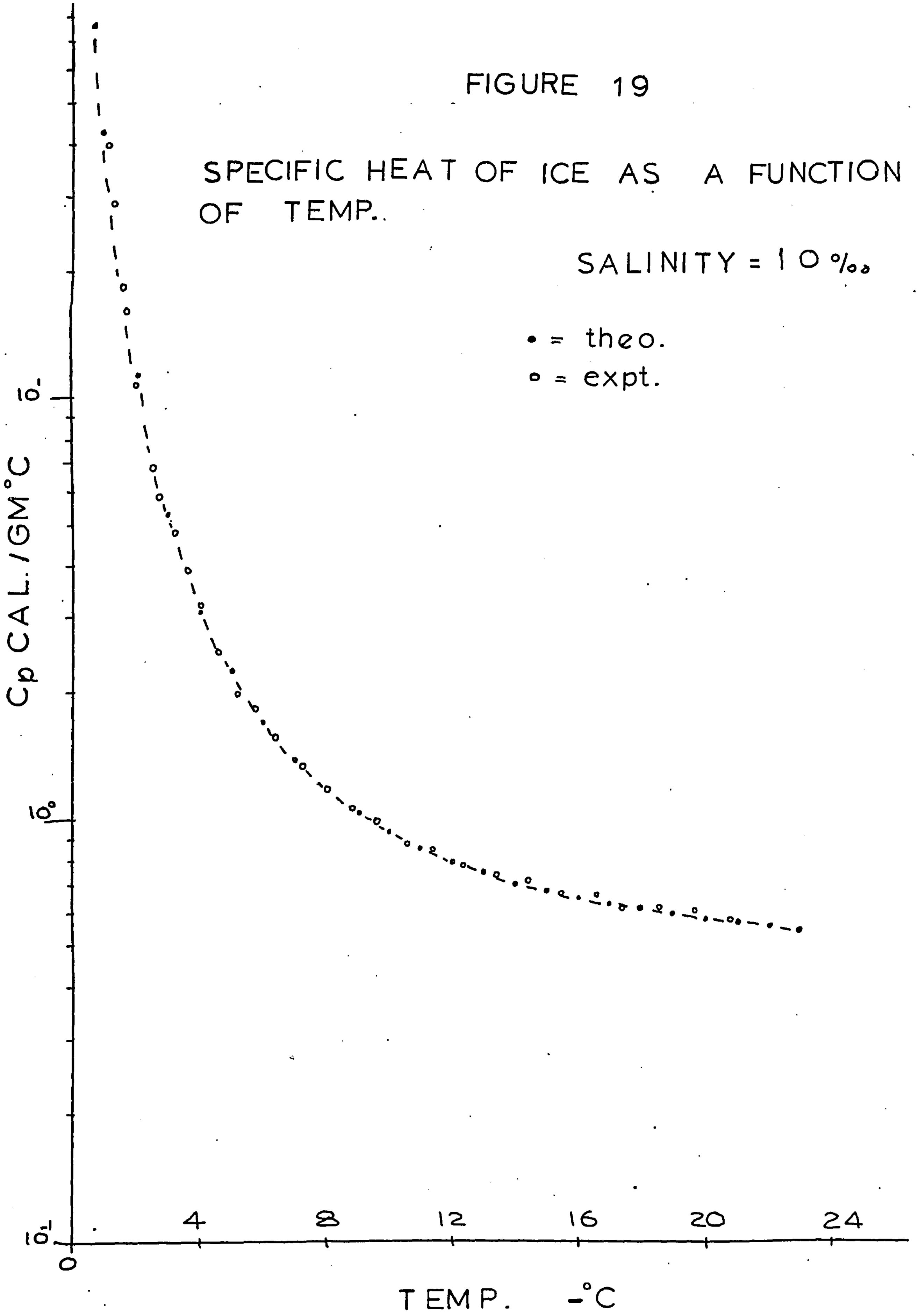


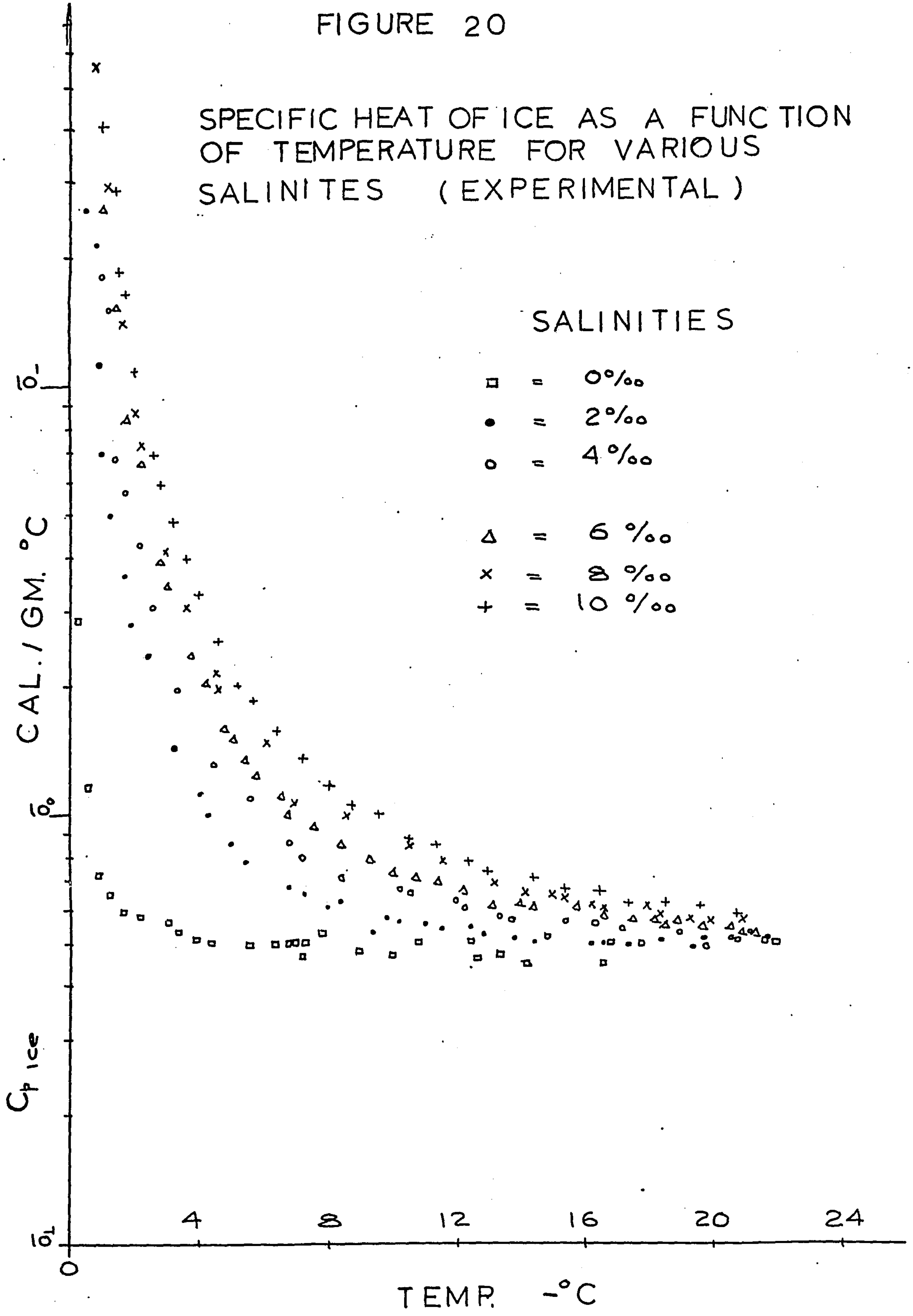
FIGURE 19

SPECIFIC HEAT OF ICE AS A FUNCTION OF TEMP.

SALINITY = 10 ‰

FIGURE 20

SPECIFIC HEAT OF ICE AS A FUNCTION OF TEMPERATURE FOR VARIOUS SALINITES (EXPERIMENTAL)



Chapter 5 - Conclusions

Specific heat of ice was first investigated by Peterson in 1883. Since then Dickinson, Osborne et al have done extensive research on the specific heat of pure ice. Malmgren, in 1925, began investigating specific heat of saline ice on board the "Maud" in the Norwegian north polar expedition of 1918. His calculation neglected the effect of brine inclusions in the sea ice. Later, in the 1950's Ono, Schwerdtfeger, Pounder and others did more work on the specific heat of sea ice. In these later works, brine inclusion was considered and also the fact that there is no real latent heat of fusion for saline ice, as there is always some phase transition involved in any temperature change.

Schwerdtfeger, in 1962, developed a theoretical relationship to determine the specific heat of saline ice and this study examined his theoretical model. The present work involved the experimental determination of the specific heat of ice as a function of temperature. The specific heat was determined for a temperature ranging from -23°C to the melting point of ice. Ice of several salinities, varying from 0 to 10°/oo, were considered.

In this study, a very close correlation between the theoretical and the experimental values was noted. That is to say, the experimental evidence verified the values of specific heat determined from the theoretical model postulated by Schwerdtfeger. The experimental inaccuracies of the experiment are given in Chapter 4. The largest relative error encountered in the experimentation is 11.7%.

The experimental determination of specific heat requires a tremendous amount of work and time. It is thus noted, that this work can be dispensed with and a faster and more dependable value of the specific heat can be determined by using the theoretical relationship

$$C_p = -\frac{\sigma}{\alpha T^2} L_i + \frac{\sigma}{\alpha T} \left\{ C_w - C_i \right\} + C_i (1 - \sigma)$$

for melting point $\leqslant T \leqslant -23^{\circ}C$

Where

C_p = Specific heat of saline ice

C_w = Specific heat of pure water

C_i = Specific heat of pure water ice

$= 0.5057 + 0.001863T$

L_i = Latent heat of fusion of pure water ice

$\alpha = -1.848 \times 10^{-2}\ {}^{\circ}C^{-1}$

σ = Salinity of sea ice in $^{\circ}/oo$

T = The temperature, in $^{\circ}C$, at which C_p is to be determined

This relationship is as good as the empirical results reported here and is much easier to use. The formula for the latent heat of formation is presented in Schwerdtfeger's paper (Schwerdtfeger, 1962). The verification of this will be helpful in solving for other physical properties of ice (saline or pure).

Thus, the specific heat values can now be determined, with certainty, by a theoretical formula. The theoretical relationship then rids us of cumbersome experimental techniques, and the thermal properties like specific heat, latent heat of formation and the thermal conductivity become more readily accessible. This provides for a better and a more complete solution of the heat flow and the heat budget equations.

As was indicated earlier, specific heat and thermal conductivity are major constituents of the term 'thermal diffusivity".

Thermal diffusivity = $\underline{K} = \frac{K}{C\rho}$

K = thermal conductivity

C = specific heat

ρ = density

Thermal diffusivity is a rapidly varying function of temperature, since each of the constituents is a function of temperature. K, C and ρ can change by several orders of magnitude in a small change of temperature. An easier and exact determination of the specific heat thermal conductivity and density as a function of temperature gives a precise and dependable value for thermal diffusivity. This precise temperature variation of such an important parameter will greatly enhance the progress of work on the flow of heat through ice.

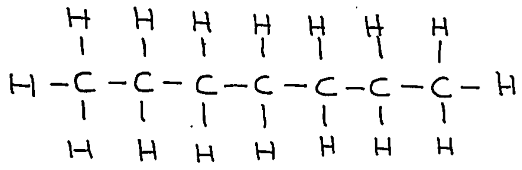
Ice under solar radiation melts and vast amounts of heat are required to melt small quantities of ice. The duration of an ice cover depends on the ability of this cover to store and conduct heat. Specific heat, the measure of the substance to store heat, is thus essential. Therefore specific heat values are of great importance in the study of the polar regions.

Appendix 1 - ^{N}-heptane

There is a need of a medium by which heat can be transported from the heat source (the heater) to all parts of the calorimeter. In this experiment, n-heptane was chosen as the calorimetric fluid. As was noted earlier, n-heptane is a pure hydrocarbon and thus does not contain any of the inorganic salts found in sea ice. Not only does it not dissolve any ice, it does not even dissolve any of the salts found in sea ice.

Normal heptane (C_7H_{16}) is a liquid in the temperature range from -90°C to + 98°C. The molecular weight is 100.2035 grams with hydrogen consisting of 16.1% and carbon the remaining 83.9% (by weight of the compound). N-heptane melts at -90.62°C and boils at +98.43°C, thus there are no phase transitions in the temperature range in which this experiment was performed.

N-heptane - $CH_3 \cdot (CH_2)_5CH_3$



$$\begin{array}{ccccccccccccccccc} & & H & & H & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & H & & H & & \end{array}$$

The specific heat of heptane as a function of temperature is needed in the calculation of the specific heat of ice. For the heat capacity of heptane the following relation holds

$$HCp = A + BT + CT^2 + DT^3 \ \frac{Cal}{deg.\ mole.}$$

Where

HCp = Heat Capacity in $\frac{\text{Cal}}{\text{deg. mole.}}$

A = 56.582

B = -0.14490

C = 5.7813 10^{-4}

D = -4.1667 10^{-7}

for a temperature of T = 240° to 370°K

Since the specific heat is defined as the heat capacity per gram of substance, the specific heat of heptane can easily be obtained by dividing HCp by the formula weight of heptane.

Table 8 and Fig. 21 show the values of the specific heat of n-heptane as determined from the above formula as a function of temperature. The information on heptane was obtained from Riddick and Bunger (1970); Perry's handbook of chemical engineering (1963) and research project No. 44 of the A.P.I.

TABLE 8

Specific heat of n-heptane as a function of temperature

Temperature		Sp. ht. hep.
°K	°C	Cal/gm°C
248.16	-25.00	0.4976
249.16	-24.00	0.4982
250.16	-23.00	0.4989
251.16	-22.00	0.4995
252.16	-21.00	0.5002
253.16	-20.00	0.5009
254.16	-19.00	0.5015
255.16	-18.00	0.5022
256.16	-17.00	0.5029
257.16	-16.00	0.5036
258.16	-15.00	0.5043
259.16	-14.00	0.5050
260.16	-13.00	0.5057
261.16	-12.00	0.5064
262.16	-11.00	0.5072
263.16	-10.00	0.5079
264.16	- 9.00	0.5086
265.16	- 8.00	0.5093
266.16	- 7.00	0.5101
267.16	- 6.00	0.5108

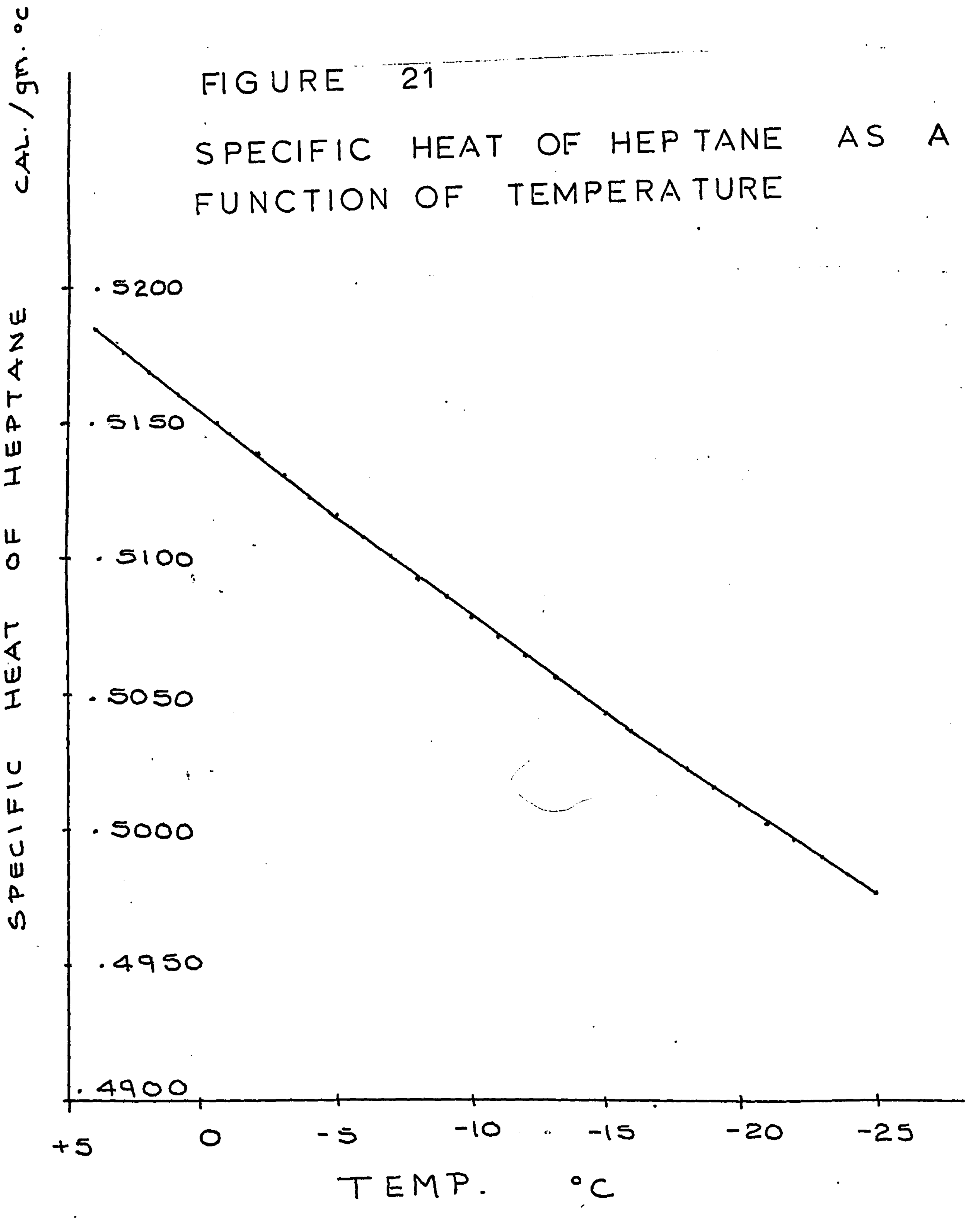
TABLE 8 cont.

Specific heat of n-heptane as a function of temperature

Temperature		Sp. ht. hep
°K	°C	Cal/gm°C
268.16	-5.00	0.5116
269.16	-4.00	0.5123
270.16	-3.00	0.5131
271.16	-2.00	0.5139
272.16	-1.00	0.5146
273.16	0.00	0.5154
274.16	+1.00	0.5162
275.16	+2.00	0.5169
276.16	+3.00	0.5177
277.16	+4.00	0.5185

FIGURE 21

SPECIFIC HEAT OF HEPTANE AS A FUNCTION OF TEMPERATURE



APPENDIX 2 - THERMOCOUPLES

The thermocouples are a good heat sink as they can carry heat from the dewar (hot) to the cold room (cold). Thus it is desirable to choose metals that have low thermal conductivity. Initially copper-constantan thermocouples were used but this choice was not satisfactory as copper is a good conductor of heat. The choice of iron-constantan thermocouples is better since iron has lower thermal conductivity. The thinnest gauge (30 gauge) available was used, again to reduce the heat leakage.

In the experiment, iron-constantan thermocouples HF/D-30-J, from 'Thermoelectric Canada Limited' were used. The thermocouples were calibrated by using secondary standards like the freezing and melting point of certain substances. According to Lange (1952) the melting and freezing temperatures are:

Name	Temperature
Heptanoic Acid ($CH_3(CH_2)_5COOH$)	- 7.5 °c melting point
Mercury (Hg)	-38.87°c freezing point
Carbon tetrachloride (CCl_4)	-22.9 °c melting point
Benzene (C_6H_6)	+ 5.5 °c melting point

The voltage was measured by putting one end of the thermocouples in the above chemicals (at their melting or freezing temperatures) and the other end at a reference temperature, which was a well stirred ice bath. In a repeated series of experiments there was a very close correlation with the values obtained from the conversion table for iron constantan thermocouples (Leeds and Northrup publication No. 077989). Also the relationship of $50\mu v/^{o}C$ for these thermocouples was verified for a temperature range of $-25^{o}C$ to $+5^{o}C$.

The close agreement between the experimental values and the values from the tables was sufficient to justify the use of the tables.

To ensure an excellent junction between the iron and constantan wires, the junctions were hard (silver) soldered. Initial plan was to use a rotary switch to switch different thermocouples to the measuring instruments. However, this switching produced spurious changes in the Emf generated by the thermocouples. This switching of the thermocouples was abandoned and extreme care was taken to ensure that the junction of the thermocouple to the measuring instrument was at a constant temperature.

APPENDIX 3 - SEA ICE

At least forty-four elements have been detected in sea water (Sverdrup et al, 1942) but only six ions (Na^+, Mg^{++}, K^+, Ca^{++}, $SO_4^=$, Cl^-) account for more than 99% of the dissolved solids. In these experiments the recipe for making the saline water was as follows:

Salt	Amount (gms)
$NaCl$	23.48
$MgCl_2$	4.98
Na_2SO_4	3.92
$CaCl_2$	1.10
KCl	0.66
$NaHCO_3$	0.19
Others*	0.15
Total	34.48

The above salts in 965.52 gms. of pure and distilled water will produce one kilogram of sea water of 34.48°/oo salinity. In nature one rarely encounters ice of salinity greater than 10°/oo, thus only a fraction of the salt will be used. For example, one needs only 4 gms. of 'sea salt' to produce two litres of sea water of 2°/oo salinity.

After the preparation of the sea ice, the salinity of the sample used was determined by two distinct methods.

The first method was one of titration. This is adequately described in Kolthoff and Sandell (1952). The Mohr titration is a delicate titration and gives the amount of silver nitrate ($AgNO_3$) needed to titrate a given amount of chlorides (using potassium

---

* Others includes trace salts as potassium bromide, sodium fluoride, strontium chloride and lithium chloride in small quantities.

chromate, K_2CrO_4, as an indicator). The salinity is determined from the chlorinity by using Knudsen's rule of constancy of occurrence. The salinity obtained in this fashion is good to ± 0.2°/oo.

Thus:

$$S^{o}/oo = 1.805 \text{ cl (in } ^{o}/oo) + 0.03$$

The second method was to determine the salinity of a sample by using the 'Hytech salinometer'. The salinometer determined the salinity of a sample by measuring the conductivity ratio for an unknown and known sample. The known sample being Copenhagen sea water of salinity 35.0001°/oo. The salinity of the unknown sample was determined by looking at conductivity ratio , corrected for temperature. This method has an accuracy of ± 0.001°/oo.

The salinity determined by the salinometer and by titration agreed very closely for the strength of the prepared solution.

APPENDIX 4 - ERROR ANALYSIS

The heat supplied by the heater is absorbed by several different elements in the apparatus, namely the heptane, the saline ice, the calorimeter plus the heat losses.

Thus:

$$\underset{\text{Heater}}{Q_{in}} = \underset{\text{Ice}}{Q_{in}} + \underset{\text{hep.}}{Q_{in}} + \underset{\text{Dewar}}{Q_{in}} + \underset{\text{losses}}{Q}$$

$$\gamma\, v i t = m_i C_p \delta |T_2 - T_1| + m_H C_H \delta |T_2 - T_1| + H \delta |T_2 - T_1| + \left(\frac{dQ}{dt}\right)(t_1 + t)$$

γ = 0.23889 cal/j to convert joules to calories

v = voltage across the heater (volts)

i = current through the heater (amps)

t = time for heating (sec.)

t_1 = time to reach equilibrium - after heating stopped (sec.)

m_i = mass of ice (gm.)

m_H = mass of heptane (gm.)

H = heat capacity of dewar $\left(\frac{\text{Cal}}{^\circ\text{C}}\right)$

C_p = specific heat of saline ice $\left(\frac{\text{Cal}}{\text{gm}^\circ\text{C}}\right)$

C_H = specific heat of heptane (Cal/gm°C)

T_1 = initial temperature of sample (μv)

T_2 = final temperature of sample (μv)

δ = 0.02 °c/μv - to convert μv to °C

$\left(\frac{dQ}{dt}\right)$ = cooling rate (Cal/sec) or

$$C_p = \left\{ \gamma v i t + m_H C_H \delta |T_2 - T_1| - H \delta |T_2 - T_1| - \frac{dQ}{dt}(t + t_1) \right\}$$

$$/ \left\{ m_i \delta |T_2 - T_1| \right\}$$

And finally

$$C_p = \frac{\gamma v i t}{\delta |T_2 - T_1| m_i} - \left(\frac{m_H}{m_i}\right) C_H - \frac{H}{m_i}$$

$$- \frac{(dQ/dt)(t + t_1)}{m_i \delta |T_2 - T_1|} \qquad (19)$$

Then

$$d C_p = \frac{1}{m_i \delta |T_2 - T_1|} \left\{ \gamma v i dt + \gamma v t di + \gamma i t dv \right.$$

$$\left. - 2 \left(\frac{dQ}{dt}\right) dt \right\} + \frac{\gamma v i t}{\delta |T_2 - T_1|} m_i^{-2} d m_i + \frac{\gamma v i t}{\delta m_i} |T_2 - T_1|^{-2} d T_1$$

$$+ \frac{\gamma v i t}{\delta m_i} |T_2 - T_1|^{-2} d T_2 + \frac{d m_H}{m_i} C_H + m_H C_H m_i^{-2} d m_i + \frac{d H}{m_i} + H m_i^{-2} d m_i$$

$$- \left(\frac{dQ}{dt}\right)(t + t_1) \left\{ \frac{m_i^{-2} d m_i}{\delta |T_2 - T_1|} + \frac{2 |T_2 - T_1|^{-2} d T_2}{\delta m_i} \right] \qquad (20)$$

Where d__ - is the error in each component's measurement

Thus

$$C_p \text{ possible error} = \frac{d C_p}{C_p} \times 100\% = \frac{(20)}{(19)} \times 100\%$$

The individual errors dm_i, etc. are obtained from noting the inaccuracies of each instrument used to measure the particular quantity. The inaccuracies of two of the instruments used is given below to illustrate the magnitude of these inaccuracies.

A. Honeywell Chart Recorder Electronik 19

- this machine, when calibrated, has a possible error in measurement of 0.25% of the span. That is to say, on the 0.1 mv scale, the error in measurement is 0.25 μV.

B. Leeds and Northrup differential Potentiometer No. 7564

- the accuracy of this instrument on the 0.016V scale is ± (60 ppm ± 0.5 μv). The accuracy quoted is for the 'worst case' i.e. if all the factors influencing the deviation act simultaneously and in the same direction, and if a 3σ confidence level is used.

Most or all the measurements were done on these two instruments, thus the tolerances of these instruments are given.

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