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Freezing Point of Seawater¹

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ABSTRACT

Accurate values of the freezing point of seawater are necessary for considering thermal processes at high latitudes and for relating the ice-water equilibrium to the thermodynamics of water in seawater at low temperature. Measurements of the freezing point of seawater at various salinities were made using three independent techniques. The results obtained by a super-cooling method were not reliable, whereas values based on a flow and an equilibration technique were indistinguishable. The effect of pressure on the freezing point of seawater was calculated from thermodynamic considerations. The variation in the freezing point temperature (T_f) with salinity ($S^{\circ}/_{\infty}$) and hydrostatic depth in meters (z) is given by:

$$T_f(^{\circ}\text{C}) = -0.0137 - 0.051990 S^{\circ}/_{\infty} - 0.0007225 (S^{\circ}/_{\infty})^2 - 0.000758 z$$

The expression is valid for seawater with salinity in the range 4–40‰ and at depths from 0–500 m provided that the relative proportions of the major constituents are characteristic of open ocean waters. Application of this relationship to temperature distributions on the Ross Ice Shelf show that seawater between 300 and 600 m has an *in situ* temperature which is up to 0.08°C below the atmospheric pressure freezing point.

1. INTRODUCTION. The freezing point of seawater is that temperature, T_f , at which pure ice and seawater are in thermodynamic equilibrium. This temperature decreases with increasing salinity and with increasing pressure. Knowledge of the freezing point of seawater is useful chemically in considering the thermodynamics of water molecules in seawater and oceanographically in considering thermal processes at high latitudes. Freezing point data provide a measurement of the free energy, or chemical potential, of water molecules in seawater. Accurate values of these parameters are useful, therefore, in evaluating the vapor pressure and osmotic pressure of seawater at low temperature, and they may be applied to considerations of the effect of ions on the free energy of water molecules in the medium.

Seawater near the ice shelves of Antarctica has been found at depths of 200–500 m which is cooled below its atmospheric freezing point (Countryman,

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2. Deceased: March, 1974.

Table I. Freezing point, T_f , of 36.5‰ salinity seawater based on previous studies. The uncertainties represent the precision of the values (approximately one standard deviation).

Source	Method	T_f (°C)
Pettersson (1883)	Supercooling	-2.04
Hansen (1904)	Flow	-1.996 ± 0.003
Miyake (1939)	Supercooling	-2.075 ± 0.005

1970; Gordon, 1971). These so-called "supercooled" waters are believed to result from either the melting of ice or freezing of water at depths where the *in situ* pressure lowers the freezing point below that of one atm. This cooling of seawater by contact with ice at depths of several hundred meters could provide a mechanism for producing dense bottom water in which its properties when "formed" (i.e., when it acquired its coldest temperature) are not characteristic of the sea surface (i.e., dissolved gas content and nutrient concentrations). The quantity of water which might be formed in this manner is highly dependent on the values used for the atmospheric freezing point of seawater.

Prior to this study there had been three investigations of the freezing point of seawater. Pettersson (1883) determined the freezing point temperature after supercooling seawater by about 0.2 to 0.3°C and nucleating it with a crystal of snow. Hansen (1904), using a flow technique developed by Prytz (1902), measured the freezing point of the seawater samples which had provided the basis for the specific gravity-chlorinity relationship of the Hydrographical Tables (Knudsen, 1901). Hansen's data were reported by Knudsen (1903), who is frequently credited with the work, though Hansen's original report provides an excellent account of the experimental methods and of the data analysis. The third investigation was conducted by Miyake (1939), who determined the freezing point by a supercooling technique. The results of these three studies are summarized in Table I.

A systematic difference of up to 0.08°C exists in the data of Hansen and of Miyake for the normal range of ocean salinities. This discrepancy is large compared to the precision of the two studies and compared to modern thermometric and oceanographic capabilities. The difference in these two sets of data has led to uncertainties in the analysis of "supercooled" seawater on the Ross and Weddell Shelves. Gordon (1971) preferred the use of Miyake's data, because it gave the most conservative estimate of subsurface cooling by the melting or freezing of ice at depths of 200–500 m. Countryman (1970), on the other hand, argued that Hansen's values were more consistent with surface field measurements of ocean temperatures near ice.

Our objective in this study was to provide more reliable values for this basic property of seawater. The discrepancies in Table I can not be attributed to world wide variations in the composition of seawater, because recent studies have shown a high degree of constancy in the chlorinity ratios of the major com-

ponents of seawater (see Pytkowicz and Kester, 1971, for a comparative summary of these analyses). The most likely causes of these differences in T_f are thermometric calibration and systematic errors inherent in the methods. Our approach has been to compare the freezing points obtained by the supercooling method, by the flow technique which Hansen used, and by an equilibration method we developed. We obtained a new relationship for the salinity dependence of the freezing point of seawater at atmospheric pressure, and then extended it using thermodynamic relationships to provide the *in situ* T_f as a function of depth.

2. EXPERIMENTAL METHODS. The basic quantities measured in this study were temperature, salinity by inductive electrical conductivity, and chlorinity by silver nitrate titration. The temperature measurements were made with a quartz crystal thermometer (QCT) (Hewlett-Packard Model 2801A). The QCT was calibrated with a platinum resistance thermometer and Mueller bridge traceable to the U.S. National Bureau of Standards. The icepoint of distilled-deionized water provided the reference temperature for the measurements. The distilled water was obtained from a block tin still and then passed through two Barnstead (DO 803) deionized columns. This water had a specific conductivity of less than $1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ at 25°C . The ice point was established by filling a 660 ml Dewar flask with crushed, distilled water, ice and then filling the interstices of the crushed ice with distilled water. The QCT probe was then immersed to a depth of 12 cm into the ice-point bath. In order to minimize the thermal hysteresis characteristics of the QCT it was cycled between 0 and 10°C several times to verify reproducible ice points before transferring to the chilled seawater systems for the freezing point measurements. The consistency of the ice-point reference temperature determined in this manner can be demonstrated by two examples. In a series of measurements with one QCT probe, five independent ice-points were measured over a three day period; these values had a standard deviation of 0.0003°C . For another QCT probe 13 ice-points over a 14 day period yielded a standard deviation of 0.0011°C . The increased variability in ice-point reference temperatures over a longer period of time most likely reflects shifts in the oscillation frequency of the quartz crystal sensor and in the measurement circuitry.

In order to provide an operational verification of our thermometric system we measured the freezing point of a sodium chloride solution for comparison with the data of Scatchard and Prentiss (1933). These measurements were made using the flow technique of Prytz (1902), which will be described in a subsequent section. The NaCl solution was 0.4970 molal and prepared by weight from J. T. Baker Reagent Grade NaCl and distilled-deionized water. Our freezing point for this solution was -1.682°C with an uncertainty of $\pm 0.001^\circ\text{C}$ due to the thermometric measurements and calibration. Interpolation of the data of Scatchard and Prentiss (1933) to this molality of NaCl

yields a freezing point of -1.6817°C . The agreement of these values for a NaCl solution shows that our apparatus and techniques yield freezing point values which are consistent with the presently accepted data for simple electrolyte solutions.

The ice point is defined as the equilibrium temperature between ice and water which is saturated with air at 1 atm pressure; this temperature is 0.000°C (Corruccini, 1968). Accordingly, the freezing points determined in this work apply to solutions which contain atmospheric gases. At equilibrium with air pure water contains 1.30 mmol of dissolved gases per kilogram of solution, whereas 35‰ salinity seawater contains $1.03 \text{ mmol kg}^{-1}$ of dissolved atmospheric gases at its freezing point (Kester, 1974). These dissolved gases produce a freezing point lowering of 0.0024°C for pure water and 0.0019°C for the seawater. Thus, in considering the freezing point depression of seawater to within a thousandth of a degree Celsius the effect of dissolved atmospheric gases cancels out between the seawater measurement and the pure water reference point, so that the freezing point lowering in degrees Celsius is due to the solutes other than air.

Salinity determinations in this work were based primarily on measurements with an Industrial Instruments Model RS-7A inductive salinometer relative to I.A.P.S.O. Standard Sea Water (Copenhagen water) using the International Oceanographic Tables (UNESCO, 1966). In order to assure that the freezing point-salinity relationship determined in this work for seawater of normal composition would not depend on the method of determining the salinity, chlorinity titrations were run on selected samples over the entire range of salinities examined. These silver nitrate titrations were done by weight using a dichlorofluorescein indicator and a dextrin dispersant; the AgNO_3 was standardized with I.A.P.S.O. Standard Sea Water. Chlorinity was related to salinity by $S_{\text{‰}} = 1.80655 \text{ Cl}_{\text{‰}}$ (UNESCO, 1966). The chlorinity and salinometer measurements provided consistent determinations of salinity to within 0.02‰ salinity over the range 4–40‰ salinity. The seawater used in the freezing point measurements was collected from one meter beneath the surface in the Sargasso Sea (34°N , 66°W). Its original salinity was 36.6‰, and the other values were obtained by dilution with distilled-deionized water or by slow evaporation at 27°C . Isotopic variations in the composition of water are not a significant factor in these freezing point measurements; a variation of 5% in the $^{18}\text{O}/^{16}\text{O}$ ratio would produce a 0.001°C change in the freezing point (Pupezin, *et al.*, 1972), whereas natural variations in this ratio are less than 2% (Craig and Gordon, 1965). Deuterium is even less significant because of its smaller abundance.

3. FREEZING POINT OF SEAWATER DETERMINED BY SUPERCOOLING. The supercooling apparatus consisted of a 500 ml Erlenmeyer flask immersed to the neck in a constant temperature bath maintained below the freezing point of the

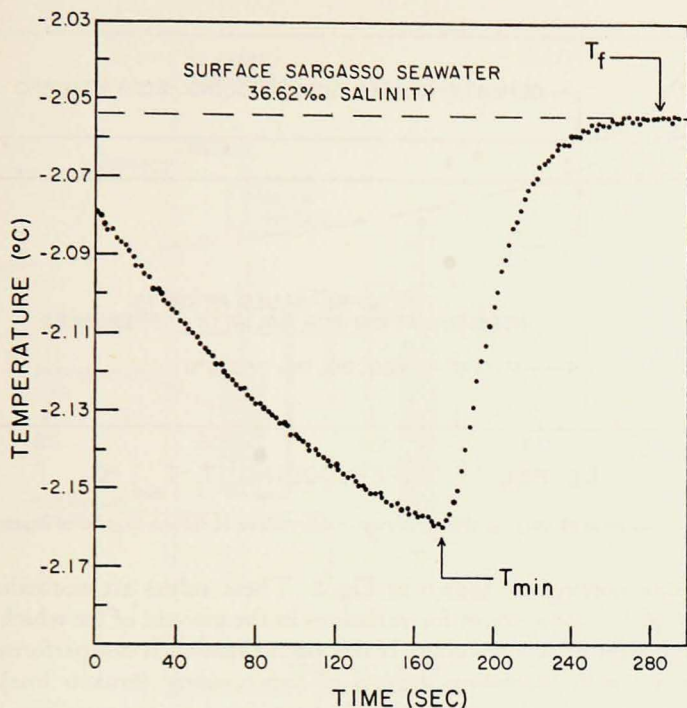


Figure 1. Supercooling curve for seawater. A particle of ice was added at 150 sec to produce nucleation.

sample. The sample was mixed by a direct-drive stirrer and the temperature was monitored to within 0.001°C at the rate of once a second with a QCT probe. After obtaining a selected degree of supercooling relative to Hansen's values, a small piece of ice was added to cause nucleation. An example of a supercooling curve is shown in Fig. 1. The freezing point was taken to be the temperature which remained constant to within 0.001°C over a 30 second period. The degree of supercooling is given by $T_f - T_{\min}$.

One of the difficulties with the supercooling technique is determining the salinity which corresponds to the thermal plateau, because of the continual removal of water from the seawater by freezing. We obtained this salinity by two methods. First, we rapidly withdrew a portion of the sample but none of the ice, and measured its salinity with an inductive salinometer. Second, we calculated the ice which must have formed, and hence the salinity after freezing, based on a heat budget and on the rise from T_{\min} to T_f . These two salinities agreed to within about 0.04‰ which corresponds to an uncertainty of 0.002°C in T_f .

The results of some freezing point measurements determined at various

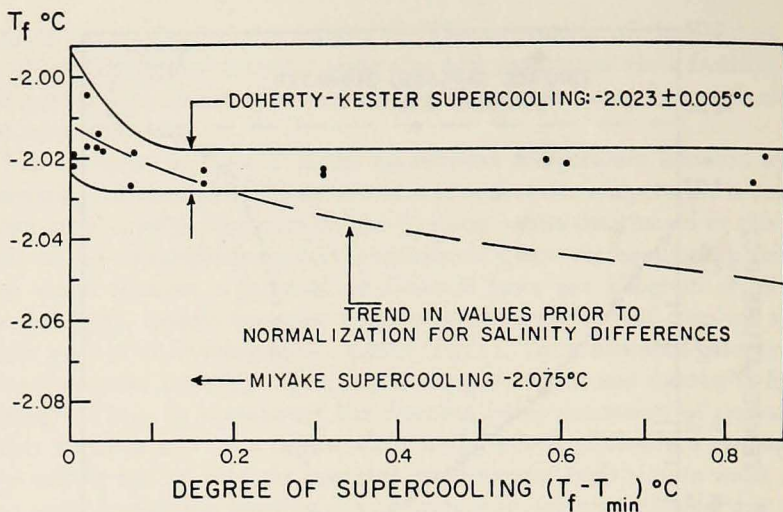


Figure 2. Freezing point of 36.5‰ salinity seawater determined at various degrees of supercooling.

degrees of supercooling are shown in Fig. 2. These values are normalized to a salinity of 36.5‰ to account for variations in the amount of ice which forms at different degrees of supercooling. If this normalization is not performed the values decrease with increasing degrees of supercooling (broken line). Our results indicate considerable scatter in T_f determined by supercooling with a possible trend to higher values at degrees of supercooling less than 0.1°C.

If one assumes that Pettersson (1883) did not apply a salinity correction for the water frozen out, his results at 0.2 to 0.3°C of supercooling agree to within 0.01°C of this work (cf. Table I and Fig. 2). Miyake's (1939) value by supercooling is about 0.05°C lower than ours. Miyake stated: "The freezing point was determined from the tangent of the [temperature versus time] curve after the state of supercooling was broken." No information is provided concerning the shape of this curve, the degree of supercooling, or the change in salinity upon freezing. We suspect that his values are unreliable due to some systematic error. With supercooling measurements there is no control over the quality of ice which forms, and errors due to brine entrapment and surface effects are possible when this method is applied to the freezing point of seawater. It is likely that the ice crystals are in contact with solutions other than the bulk sample due to the incorporation of various solutes in the ice (Workman and Reynolds, 1950; Paren and Walker, 1971; Seidensticker, 1972).

4. FREEZING POINT OF SEAWATER BY THE FLOW METHOD. Measurements of the freezing point of seawater were made with a flow technique similar to the one used by Hansen (1904). In this method seawater flows by gravity from a reservoir through a precooling coil and then through a freezing point coil

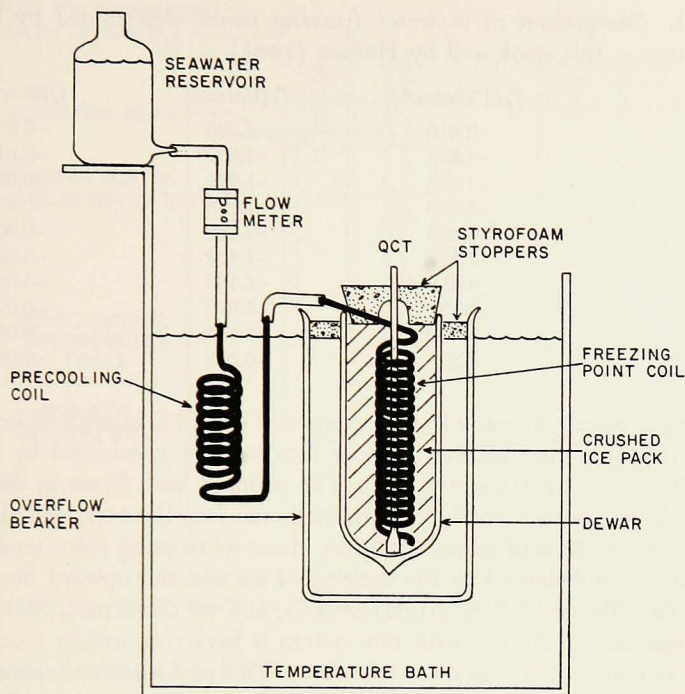


Figure 3. Apparatus for determining the freezing point of seawater by the flow method.

immersed in crushed ice. The seawater enters the base of the crushed ice pack contained in a 660 ml Dewar flask, and then percolates upward through the ice and around the second coil overflowing into an outer beaker (Fig. 3). The temperature of the seawater-crushed ice pack was measured at the base of the Dewar by a QCT probe which was located inside the freezing point coil. With this method seawater is precooled to 0.02 to 0.06°C above its freezing point by the coil in the temperature bath, and it then contacts ice in the base of the Dewar flask which is initially at 0°C . The mixing of seawater and ice above the freezing point temperature results in a melting of some of the ice and a cooling of the Dewar flask and its contents until the freezing point is reached. In our experiments the seawater flowed at $5\text{--}6\text{ ml min}^{-1}$ until the Dewar flask overflowed. The flow rate was then adjusted to $0.4\text{--}0.7\text{ ml min}^{-1}$ until the temperature remained constant to within $\pm 0.0002^{\circ}\text{C}$ for 25 minutes. The flow was then terminated and the temperature decreased by at most 0.0005°C and remained constant for 20–30 minutes. This stable temperature was taken as the freezing point at the salinity of the seawater in the reservoir.

The primary requirement of this method is that the constant temperature reached represents a true equilibrium between the initial seawater and ice, and

Table II. Comparison of seawater freezing points determined by the flow technique in this work and by Hansen (1904).

Salinity	T_f (This work)	T_f (Hansen)	Difference
36.52	-2.010	-1.996	-0.014
35.49	-1.950	-1.937	-0.013
34.50	-1.894	-1.881	-0.013
33.00	-1.808	-1.796	-0.012
30.00	-1.637	-1.628	-0.009
27.01	-1.471	-1.462	-0.009
22.01	-1.195	-1.186	-0.009
16.99	-0.920	-0.913	-0.007
11.97	-0.649	-0.642	-0.007
6.97	-0.381	-0.373	-0.008

that it is not merely a steady state temperature due to a balance of heat fluxes and a dilution of the seawater. These factors were considered in detail by Prytz (1902) and by Hansen (1904). The primary heat fluxes in the Dewar flask are by downward conduction through the ice, the coil, and the QCT probe and by the flow of seawater slightly above its freezing point temperature. These fluxes are balanced by the melting of ice and the upward flow of seawater outside the coil. Prytz (1902) showed, and we confirmed, that the constant temperature achieved with this system is invariant within 0.0005°C to the flow rate over the range $0-10 \text{ ml min}^{-1}$. This performance depends largely on the effectiveness of the precooling coil, and in our system the bath temperature was regulated to a few hundredths of a degree above the QCT temperature. Hansen (1904) sampled the seawater in the base of the Dewar after the constant temperature was reached and found that its dilution by melting ice was less than 0.01‰ salinity. The agreement of our measurements of the freezing point of an NaCl solution with the data of Scatchard and Prentiss (1933) provides further evidence that this technique produces accurate results.

The flow method was used to determine the freezing point of seawater over the range 7 to 36.5‰ salinity. The range between duplicate measurements was consistently within 0.001°C which represented the precision of this method. A comparison of our measurements with Hansen's freezing point relationship is given in Table II. Our values of T_f are systematically lower than Hansen's by 0.013°C in the oceanic range of salinities. Some discrepancy between the two sets of data could arise from the calibration of thermometric and salinity measurements. The most likely source of error in the flow method is the presence of heat fluxes in the Dewar flask. Both a steady state temperature, as opposed to an equilibrium temperature, and dilution by melting ice will yield values higher than T_f ; hence, the lowest temperature obtained by this method is likely to be the closest to T_f . In order to provide stronger evidence for the absence of systematic errors in our measurements of T_f by the flow technique it is useful to consider an independent method.

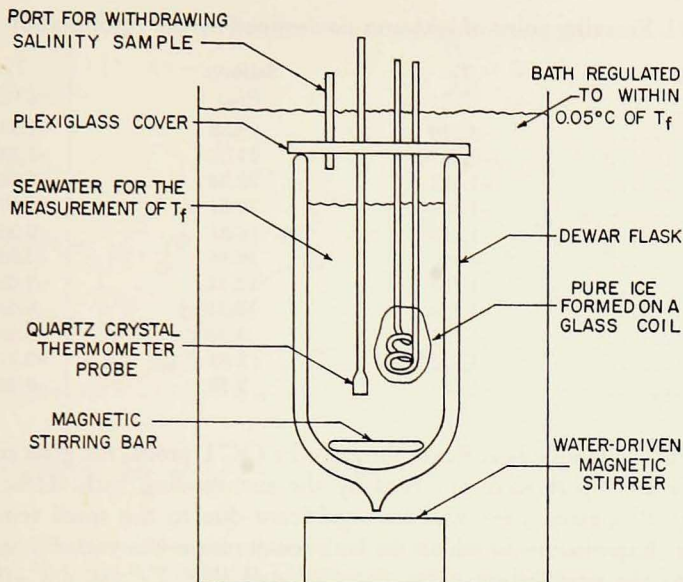


Figure 4. Apparatus for determining the freezing point of seawater by an equilibration method.

5. FREEZING POINT OF SEAWATER BY AN EQUILIBRATION TECHNIQUE. The concept of an equilibration method was previously employed by Walker and Robertson (1902) and by Scatchard *et al.* (1932). In our application the equilibration technique is analogous to a solubility measurement in that pure ice without visual defects (such as air bubbles and stress cracks) is placed in contact with seawater under nearly adiabatic conditions. The temperature of the seawater is monitored until a constant value is reached. The seawater then is withdrawn and its salinity is determined. The equilibration technique has the advantages that (i) the dilution of the seawater by melting ice is accounted for in the final salinity measurement, (ii) it avoids the problem of brine entrapment in the ice encountered with supercooling, and (iii) if done with care it is not subject to a steady state masquerading as an equilibrium. The apparatus used is illustrated in Fig. 4. Optically clear ice was prepared by pumping an ethylene glycol solution at -10°C through a glass coil immersed in distilled-deionized water. Seawater chilled to about 0.5°C above its freezing point was added to the Dewar flask containing the ice and a QCT probe and was stirred to reach thermal equilibrium. The entire system was immersed in a temperature bath regulated to within 0.05°C of the QCT temperature in order to minimize heat fluxes with the surroundings. With this method ice melted until the temperature reached T_f , which was indicated by a value which was constant to within $\pm 0.0005^\circ\text{C}$ for 30 minutes. After reaching this temperature 200 ml of the seawater were withdrawn and the salinity was determined.

Table III Freezing point of seawater determined by the equilibration method.

Salinity (‰)	T_f (°C)	Salinity (‰)	T_f (°C)
40.20.....	-2.220	24.59	-1.333
39.75.....	-2.197	24.53	-1.330
36.96.....	-2.032	20.04	-1.086
36.18.....	-1.990	19.81	-1.072
35.06.....	-1.925	16.81	-0.906
34.90.....	-1.916	16.44	-0.886
34.42.....	-1.888	12.33	-0.665
32.14.....	-1.758	11.95	-0.648
31.65.....	-1.731	8.38	-0.457
30.22.....	-1.652	3.83	-0.213
28.15.....	-1.535	3.78	-0.208

With this technique heat fluxes through the QCT probe, the glass coil tubes, and the sample port were absorbed by the surrounding bath. Heat transfer across the Plexiglass cover was not significant due to the small temperature difference. Experiments in which the bath temperature was varied intentionally relative to the equilibrium value demonstrated that T_f was not affected as long as the bath was within 0.1°C of T_f . The internal sources of heat from the QCT probe and the mechanical stirring did not affect the temperature equilibrium; if these were significant, ice would melt diluting the sample and producing an upward drift in temperature. The freezing points determined by this method for salinities between 3.8 and 40.2‰ are given in Table III.

6. DISCUSSION OF THE RESULTS. While our work was in progress another set of recent freezing point measurements by L. A. Murray (formerly Mayneord) and C. N. Murray was reported (Riley and Chester, 1971, p. 35). Their experimental technique was similar to the equilibration method used by us (Murray and Murray, private communication). In order to compare the experimental results of the various measurements to within 0.001°C over a range of 2°C (salinities $0\text{--}40\text{‰}$), it is useful to consider deviations from a common reference relationship rather than the absolute values. Accordingly, we arbitrarily selected a reference temperature, T_{ref} , which was a linear function of salinity:

$$T_{\text{ref}} = -0.05522 S\text{‰} \quad (1)$$

Comparisons between the different sets of data were then made by examining $T_f - T_{\text{ref}}$ as a function of salinity. The results are shown in Fig. 5.

The agreement between the flow and equilibration measurements in this work is within $\pm 0.002^\circ\text{C}$ for all the experimental points. We, therefore, conclude that the flow technique is capable of reliable results when there is ade-

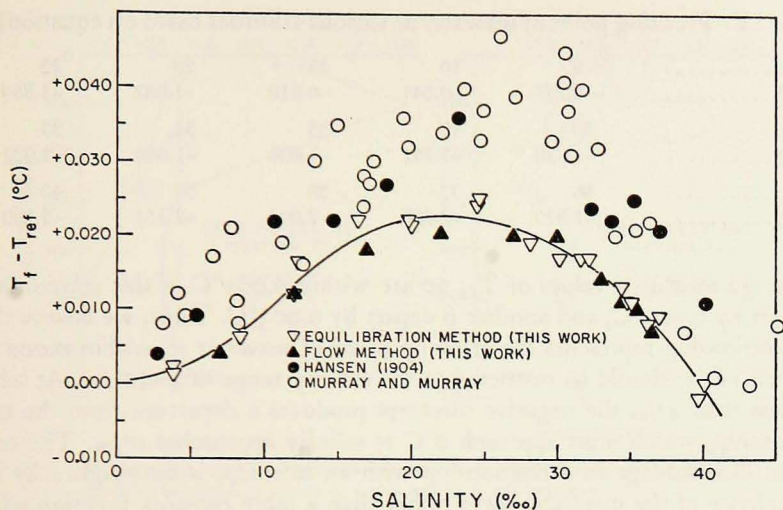


Figure 5. Comparison of four sets of freezing point data relative to the arbitrary reference temperature given by equation (1). The solid curve represents the combined results of this work.

quate precooling of the flowing seawater. The previous comparison in Table II between our work and the values of Hansen (1904) was based on Hansen's smoothed interpolation formula. His experimental data varied from 0.004 to 0.015°C higher than ours (Fig. 5). The data of Murray and Murray were also higher than ours by as much as 0.025°C and they showed a scatter of 0.015°C. We suspect that their higher values and the scatter were due to heat fluxes in their equilibration apparatus. The top of their Dewar flask was isolated from ambient temperature by a tray of ice (presumably at 0°C), whereas we found that it was necessary to maintain the temperature above the Dewar to within 0.1°C of T_f . Based on the high degree of consistency obtained by two independent methods in this work we conclude that the flow and equilibration methods provide the best results for a T_f -salinity relationship.

We previously noted that the supercooling method appeared to show a trend when extrapolated to zero degree of supercooling (Fig. 2). Such an extrapolation is subject to considerable scatter, but it agrees within 0.003°C of the $T_f = -2.008^\circ\text{C}$ obtained by the other two methods at 36.5‰ salinity. Values obtained at 0.2 to 0.8°C supercooling, however, are 0.016°C lower than the other two methods. There appears to be some source of systematic error in the supercooling technique for finite degrees of supercooling.

The freezing point data obtained by the flow and equilibration methods in this work were combined and a least squares polynomial regression was used to obtain an empirical T_f -salinity relationship:

$$T_f = -0.0137 - 0.051990 S/\text{‰} - 0.00007225 (S/\text{‰})^2 \quad (2)$$

Table IV. Freezing point of seawater at various salinities based on equation (2).

$S(‰)$	5	10	15	20	25
$T_f(^{\circ}\text{C})$	-0.275	-0.541	-0.810	-1.082	-1.359
$S(‰)$	30	32	33	34	35
$T_f(^{\circ}\text{C})$	-1.638	-1.751	-1.808	-1.865	-1.922
$S(‰)$	36	37	38	39	40
$T_f(^{\circ}\text{C})$	-1.979	-2.036	-2.094	-2.151	-2.209

Of the 32 measured values of T_f , 20 are within 0.001°C of this relationship, 6 depart by 0.002°C , and another 6 depart by 0.003°C . Thus, we believe that this relationship represents the freezing point of seawater to within 0.002°C . The use of (2) should be restricted to the salinity range of 4–40‰. At salinities less than 4‰ the negative intercept produces a departure from the true relationship, which must approach 0°C as salinity approaches $0^{\circ}/_{\infty}$. The conceptual disadvantage in a relationship with an intercept is outweighed by the convenience of the quadratic form rather than a more complex function without an intercept. Application of (2) for natural waters at salinities less than 4‰ is also questionable because of variations in the relative composition of the major components from their oceanic values. A listing of T_f at selected salinities is provided in Table IV.

7. EFFECT OF PRESSURE ON THE FREEZING POINT OF SEAWATER. In order to resolve the question of supercooled waters in the vicinity of ice submerged at depth, it is necessary to consider the effect of pressure on T_f . The change in T_f with pressure can be calculated from thermodynamic data without severe assumptions. The Clausius-Clapeyron equation provides the basis for this calculation:

$$\frac{dT_f}{dP} = T \frac{\Delta \bar{V}_f}{\Delta \bar{H}_f} \quad (3)$$

where $\Delta \bar{V}_f = \bar{V}_i - \bar{V}_w$ is the change in the molar volume of water molecules upon formation of ice, i , from liquid water, w ; $\Delta \bar{H}_f = \bar{H}_i - \bar{H}_w$ is the molar enthalpy of fusion; T is the absolute temperature. In order to calculate $d T_f/dP$

Table V. Values for the molar enthalpy \bar{H} and volume \bar{V} of water (w) and ice (i) used to calculate the pressure dependence of T_f .

Medium	T ($^{\circ}\text{C}$)	P (atm)	\bar{H}_w (cal mole $^{-1}$)	\bar{H}_i (cal mole $^{-1}$)	\bar{V}_w (cm 3 mole $^{-1}$)	\bar{V}_i (cm 3 mole $^{-1}$)	$\frac{dT_f}{dP}$ ($^{\circ}\text{C atm}^{-1}$)
Water	0.00	1.0	2748	1312	18.018	19.652	-0.00753
Seawater	-1.96	1.0	2713	1288	18.007	19.646	-0.00755
Seawater	-1.96	40.0	2713	1288	17.972	19.623	-0.00761

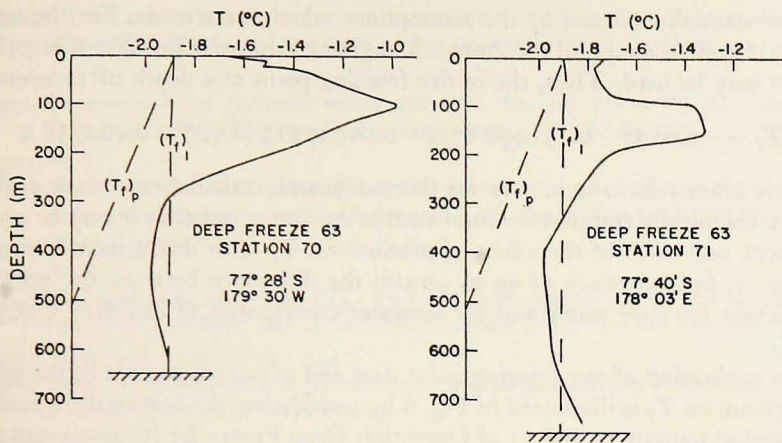


Figure 6. Relationship of vertical temperature profiles at approximately 90 km from the Ross Ice Shelf to the freezing points at 1 atm and at *in situ* pressure.

we assumed that the solutes in seawater do not affect the molar enthalpy of water molecules, \bar{H}_w , and that $\Delta\bar{H}_f$ does not vary significantly with pressure from 1 to 40 atm (Moore, 1972, p. 211). Values of the enthalpy of water and ice and of their heat capacities were obtained from Dorsey (1940, p. 265). Data on the molar volume of ice and its thermal expansion and compressibility were used to calculate \bar{V}_i (Dorsey, 1940, p. 467, 469, 471). The molar volume of water in seawater at -1.96°C and 35‰ salinity was obtained in the following manner. The partial molal volume of water in seawater (\bar{V}_w)_{sw} may be related to the molar volume of pure water (\bar{V}_w)_{pw} by:

$$(\bar{V}_w)_{sw} = \{1 - F(T)\}(\bar{V}_w)_{pw} \quad (4)$$

where the proportionality factor, $F(T)$, is a function of temperature. The partial molal volume data of Duedall and Weyl (1967) were used to obtain (\bar{V}_w)_{sw} at 5°C intervals from 0–25°C (their Table 6). The (\bar{V}_w)_{pw} at these temperatures were obtained from Dorsey (1940, p. 204–205). The $F(T)$ was evaluated at each temperature and these results were graphically extrapolated to -1.96°C at which $F(T) = 8.49 \times 10^{-4}$. The (\bar{V}_w)_{sw} at -1.96°C was then calculated from (\bar{V}_w)_{pw} at this temperature. In order to estimate (\bar{V}_w)_{pw} at -1.96°C and 40 atm, we assumed that the compressibility of seawater (Lepple and Millero, 1971) between 1 and 40 atm was mainly due to the compression of water molecules (e.g., the compression of ions and the volume changes due to shifts in ion-pairing [Kester and Pytkowicz, 1970] were ignored). The results of these calculations are shown in Table V. The pressure dependence of T_f is sufficiently insensitive to the changes in the thermodynamic parameters of water and ice over the range 0 to -2°C and 1 to 40 atm, that the results are

not substantially affected by the assumptions which were made. For the upper several hundred meters of the Antarctic region a value of $dT_f/dP = 0.00758^\circ\text{C atm}^{-1}$ may be used. Thus, the *in situ* freezing point at a depth of 1 meters is:

$$T_f = -0.0137 - 0.051990 S^\circ_{\infty} - 0.00007225 (S^\circ_{\infty})^2 - 0.000758 z \quad (5)$$

One is often reluctant to rely on thermodynamic calculations when dealing with a chemically complex medium such as seawater, and thus it may be useful to check our value of the effect of pressure on T_f with direct measurements. However, for a pressure of up to 40 atm the difference between the pressure coefficient for pure water and for seawater corresponds to less than 0.003°C in T_f .

An application of our freezing point data and of our assessment of the effect of pressure on T_f is illustrated in Fig. 6 by considering the temperature profiles obtained at stations 70 and 71 of Operation Deep Freeze 63 (Countryman and Gsell, 1966). A layer of water 300 m thick occurs at 300–600 m which has a temperature as much as 0.07°C below the one atm pressure freezing point. It is most likely that this water was cooled by contact with ice at a depth greater than 100 m. The new freezing point data obtained in this work will permit a more extensive consideration of the origin of this water which is "supercooled" relative to the one atmosphere freezing point.

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REFERENCES

- CORRUCCINI, R. J.
1968. Principles of thermometry (measurements of temperature). Treatise on Analytical Chemistry, Part I, Vol. 8, edited by I. M. Kolthoff, P. J. Elving, and E. B. Sandell. Interscience, New York, p. 4937–4990.
- COUNTRYMAN, K. A.
1970. An explanation of supercooled waters in the Ross Sea. *Deep-sea Res.*, 17: 85–90.
- COUNTRYMAN, K. A. and W. L. GSELL
1966. Operations Deep Freeze 63 and 64: Summer Oceanographic Features of the Ross Sea. U.S. Naval Oceanographic Office, Tech. Rept. No. TR-190. Washington, D.C. 193 pp.
- CRAIG, HARMON and L. I. GORDON
1965. Isotopic oceanography: Deuterium and oxygen 18 variations in the ocean and the marine atmosphere. Symposium on Marine Geochemistry, edited by D. R. Schink and J. T. Corless. Occasional Publ. No. 3, Graduate School of Oceanography, Univ. of Rhode Island, Kingston, p. 277–374.
- DORSEY, N. E.
1940. Properties of Ordinary Water Substance. Amer. Chem. Soc. Monograph Series No. 81, Reinhold, New York, 673 pp.

DUEDALL, I. W. and P. K. WEYL

1967. The partial equivalent volumes of salts in seawater. *Limnol. Oceanogr.*, 12: 52-59.

GORDON, A. L.

1971. Oceanography of Antarctic waters. Antarctic Research Series, Vol. 15, edited by J. L. Reid. Amer. Geophys. Union, Washington, D.C., p. 169-203.

HANSEN, H. J.

1904. Experimental determination of the relation between the freezing point of seawater and its specific gravity at 0°C. Meddelelser fra Kommissionen for Havundersøgelser Seris: Hydrografi, Bind I, Nr. 2, 10 pp.

KESTER, D. R.

1974. Dissolved gases other than CO₂. Chemical Oceanography, Vol. 1, second edition, edited by J. P. Riley and G. Skirrow. Academic Press, London. In press.

KESTER, D. R. and R. M. PYTKOWICZ

1970. Effect of temperature and pressure on sulfate ion association in seawater. *Geochim. Cosmochim. Acta*, 34: 1039-1051.

KNUDSEN, MARTIN

1901. Hydrographical Tables. G. E. C. Gad, Copenhagen, 63 pp.

1903. Gefrierpunktabelle für Meerwasser. *Publ. Circ. Explor. Mer*, 5: 11-13.

LEPPLE, F. K. and F. J. MILLERO

1971. The isothermal compressibility of seawater near one atmosphere. *Deep-sea Res.*, 18: 1233-1254.

MIYAKE, YASUO

1939. Chemical studies of the western Pacific Ocean. III. Freezing point, osmotic pressure, boiling point, and vapour pressure of seawater. *Bull. Chem. Soc. Japan*, 14: 58-62.

MOORE, W. J.

1972. Physical Chemistry, fourth edition. Prentice-Hall, Englewood Cliffs, New Jersey, 977 pp.

PAREN, J. G. and J. C. F. WALKER

1971. Influence of limited solubility on the electrical and mechanical properties of ice. *Nature (London) Phys. Sci.*, 230: 77-79.

PETTERSSON, OTTO

1883. On the properties of water and ice. *Vega-Expeditionens vetenskaplige Iakttagelser*, 2: 249-323.

PRYTZ, K.

1902. Methode zur Bestimmung des Gefrierpunktes einer Lösung bei konstanter Temperatur. *Ann. der Physik*, 7: 882-892.

PUPEZIN, JOVAN, GYORGY JAKLI, GABOR JANSKO, and W. ALEXANDER VAN HOOK

1972. The vapor pressure isotope effect in aqueous systems. I. H₂O—D₂O (-64° to 100°) and H₂¹⁶O—H₂¹⁸O (-17° to 16°); Ice and liquid. II. Alkali metal chloride solutions in H₂O and D₂O (-5° to 100°). *J. Phys. Chem.*, 76: 743-762.

PYTKOWICZ, R. M. and D. R. KESTER

1971. The physical chemistry of seawater. *Oceanogr. Mar. Biol. Ann. Rev.*, 9: 11-68.

RILEY, J. P. and R. CHESTER

1971. Introduction to Marine Chemistry. Academic Press, London, 465 pp.

SCATCHARD, GEORGE, P. T. JONES, and S. S. PRENTISS

1932. The freezing points of aqueous solutions. I. A freezing point apparatus. *J. Amer. Chem. Soc.*, 54: 2676-2691.

SCATCHARD, GEORGE, and S. S. PRENTISS

1933. The freezing points of aqueous solutions. IV. Potassium, sodium, and lithium chlorides and bromides. *J. Amer. Chem. Soc.*, 55: 4355-4362.

SEIDENSTICKER, R. G.

1972. Partitioning of HCl in the water-ice system. *J. Chem. Phys.*, 56: 2853-2857.

UNESCO

1966. International Oceanographic Tables. UNESCO Office of Oceanography.

WALKER, JAMES, and A. J. ROBERTSON

1902. Freezing point depression in electrolytic solutions. *Proc. Roy. Soc. Edinburgh*, 24: 363-379.

WORKMAN, E. J., and S. E. REYNOLDS

1950. Electrical phenomena occurring during the freezing of dilute aqueous solutions and their possible relation to thunderstorm electricity. *Phys. Rev.*, 78: 254-259.