PRESSURE-MELTING OF ICE

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ABSTRACT

The pressure-melting curve of ice is often found in literature dealing
with ice problems. This curve originates from the excellent experimental
works of G.Tammann (1903) and P.V.Bridgman (1912). The method used means
that ice at constant temperature is submitted to an external pressure. When
increasing the pressure a sudden volume change occurs, the pressure-melting
point is reached. Results from their works are summarized in this paper.

An alternative experimental method was used in this study. Water is con-
fined in a filled up pressure tank. The water is then cooled from an ini-
tial temperature of 0°C. The ice formed creates a pressure increase in the
ice-water mixture. At any temperature a corresponding pressure occurs at
phase equilibrium. The temperature and the pressure are measured in the
ice-water mixture. The results are in good agreement with earlier measure-
ments. The method used, which is easy to handle even with this prototype
equipment, should be more accurate than the old method since one possible
source of error (the external pressure) is eliminated. The method could be
used for other substances than pure water.

1.   BACKGROUND

At WREL the interest in pressure-melting originates from the construction
of an ice-powered cart Nordell (1986, 1987). The driving force of this cart
is the pressure-volume-work of freezing water. The cart which has a weight
of 200 kg, incl. driver, reaches a speed of about 70 km/h. The water volume
is 27 1 and the maximum pressure is limited to 25 MPa this being the maxi-

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mum strength of the pressure tank. The maximum driving distance is limited to 400 m.

Riley (1988) tells that Faraday described pressure-melting in 1860. The very first laboratory experiments on pressure-melting of ice (Ih) were performed by G. Tammann (1903), who also discovered ice II and ice III. This work was followed by F. V. Bridgman (1912).

Tammann and Bridgman used a method where a small volume of ice, at isothermal conditions, is compressed by a piston. The pressure is slowly increased and when the volume of the ice suddenly decreases the pressure-melting point is reached. This procedure is then repeated for ice at different temperatures. The excellent work of Tammann was pioneering. The pressure and the temperature were measured with an accuracy of 10 bars and 0.1 ^{o}C respectively. The phase diagrams of ice Ih and temperature-pressure data which are frequently presented in literature on ice physics originate from the works of Tammann and Bridgman. More recent measurements on melting-pressure of ice Ih have not been found.

2. AIM

The aim is to study melting-pressure of ice in the temperature range of 0°C to -22°C in a laboratory test.

The melting-pressure is seen as the maximum pressure obtained when water in a filled up, confined container is cooled below 0 ^{o}C. The lower density of the ice formed results in a pressure raise. At any constant water temperature the pressure becomes constant at phase equilibrium. A temperature increase means melting and a lowered temperature means that ice is formed until a new corresponding pressure occurs. Thus the pressure is created by the freezing water itself. The temperature and the pressure are detected in the ice-water mixture.

3. THEORY

The theory of thermodynamics gives a theoretical explanation of pressure-melting. The Clausius-Clapeyron equation (1) gives the general solution for one substance with two phases at phase equilibrium (ph.e).

$$\frac{\partial P}{\partial T}\bigg|_{ph.e} = \frac{L}{T \cdot (v_1 - v_s)} \tag{1}$$

where P (Pa) and T (K) are pressure and temperature respectively and L (J/kg = Nm/kg) is the latent heat. The specific volumes $v_x = 1/\rho_x$ (m^3/kg) where ρ_x is the density. The specific volume depends only on the changes in pressure and temperature. The liquid phase is denoted by l and s denotes the solid phase. The thermal volume change is defined at constant pressure, see eq.(2) and the compressional volume change is defined at constant temperature, eq.(3).

$$\left(\frac{\partial V}{V} = \frac{\partial v}{v} \right)_P = \alpha \cdot \partial T \qquad (2)$$

$$\left(\frac{\partial V}{V} = \frac{\partial v}{v} \right)_T = -\kappa \cdot \partial P \qquad (3)$$

The relative volume change ($\partial V/V$) is equal to the relative specific volume change ($\partial v/v$). The coefficient of thermal volume expansion is α (1/K) and κ (1/Pa) is the compressibility. To calculate the specific volume changes of two phases at phase equilibrium, eqs.(2) and (3) are added for each of the two phases. Eq.(4) and eq.(5) are the differential equations for the volume changes of the water phase (w) and the ice phase (i).

$$\frac{\partial v_w}{v_w} = \alpha_w(T) \cdot \partial T - \kappa_w(P) \cdot \partial P \qquad (4)$$

$$\frac{\partial v_i}{v_i} = \alpha_i(T) \cdot \partial T - \kappa_i(P) \cdot \partial P \qquad (5)$$

The solutions of eqs.(4) and (5) are given by the following expressions.

$$v_w = C_w \cdot e^{(A_w - K_w)} \qquad (6)$$

$$v_i = C_i \cdot e^{(A_i - K_i)} \qquad (7)$$

where $\int \alpha(T) \cdot \partial T = A + C_1$ and $\int -\kappa(P) \cdot \partial P = -K + C_2$. The constants e^{C_1} and e^{C_2}, where e is the base of the natural logarithm, result in a new constant C_x. It is presumed that the total mass (m = V/v) and the total volume (V) of water + ice are constant i.e. $\partial V = \partial m = 0$, see eq.(8) and eq.(9)

$$m = m_i + m_w = \frac{V_i}{v_i} + \frac{V_w}{v_w} = \frac{V}{v} \qquad (8)$$

$$V = V_i + V_w \qquad (9)$$

With eqs.(8) and (9) the frozen part (m_i) of the total mass ($m=1$) can be expressed:

$$m_i = \frac{v_w - v}{v_w - v_i} \qquad (10)$$

where v is the specific volume of the ice-water mixture (water) at initial conditions, $0^\circ C$ and 0 Pa. Finally, eqs.(6) and (7) into eq.(1) result in eq.(11) which defines the melting-pressure curve.

$$\frac{\partial P}{\partial T}\bigg|_{ph.e} = \frac{L}{T \cdot \left[C_w \cdot e^{(A_w - K_w)} - C_i \cdot e^{(A_i - K_i)} \right]} \qquad (11)$$

Eq.(11) is solved numerically starting at $P = 0$ (Pa) och $T = 0$ ($^\circ C$). For each pressure step, the corresponding temperature step is calculated.

The used parametric expressions of α, κ and L, listed below, are determined from regression analysis of experimental data in cited literature. Hobbs (1974) gives the latent heat of fusion, L. The thermal volume expansion of ice, α_i is from Hobbs (1974) and the corresponding value of water, α_w is found in Angell (1980), (after Zhelesnyi, 1969). The density of water from Böni (1983) and the density of ice from Bridgman (1912) at $0^\circ C$ and 0 Pa give v_w and v_i from which the integration constants are determined. The integration constants C_i and C_w are determined by solving eq.(6) and eq.(7) for the boundary condition $v(T=0,P=0)=1/\rho$.

$L = (333.6 + 5.20424 \cdot Tc + 0.03242 \cdot Tc^2) \cdot 10^3$		$(J/kg, ^\circ C)$
$\alpha_i = (161 - 0.675 \cdot Tc) \cdot 10^{-6}$		$(1/^\circ C)$
$\alpha_w = (-1.58 - 0.02943 \cdot Tc - 0.015714 \cdot Tc^2) \cdot 10^{-4}$		$(1/^\circ C)$
$\kappa_i = (3.502474 - 2.474952 \cdot 10^{-2} \cdot Pb + 5.764791 \cdot 10^{-6} \cdot Pb^2) \cdot 10^{-6}$		$(1/bar)$
$\kappa_w = (5.202 - 2.002517 \cdot 10^{-2} \cdot Pb + 6.59652 \cdot 10^{-6} \cdot Pb^2) \cdot 10^{-6}$		$(1/bar)$
$C_i = 1/\rho_i = 1/917.3$		(m^3/kg)
$C_w = 1/\rho_w = 1/999.84$		(m^3/kg)

For performed calculations the pressure step 10^4 (Pa) was used. The calculations are summarized in Table 1. The temperature, pressure, density and the volumes of the two phases are given at phase equilibrium. The calculated temperature-pressure gradient is $\partial T/\partial P = -7.369 \cdot 10^{-8}$ $^\circ C/Pa$ ($-7.369 \cdot 10^{-3}$ $^\circ C/bar$) between 0 and 10^4 Pa (0 - 0.1 bar). The calculated melting-pressure curve is presented in the diagrams of Figure 2 to facilitate a comparision with experimental data.

Table 1. Calculated melting-pressure, density and volume% of
an ice-water mixture at phase equilibria.

Temperature	pressure	density		volume	
		ice	water	ice	water
(^{o}C)	(bar)	(kg/m^3)		(%)	
+0.0	0	917.3	999.84	0.0	100.0
-1.0	134	921	1006	7.7	92.3
-2.0	264	925	1012	14.5	85.5
-3.0	390	928	1018	20.5	79.5
-4.0	513	931	1023	25.7	74.3
-5.0	632	934	1028	30.4	69.6
-6.0	747	936	1033	34.5	65.5
-7.0	860	938	1037	38.2	61.8
-8.0	969	940	1041	41.5	58.5
-9.0	1075	942	1045	44.4	55.6
-10.0	1178	943	1049	47.0	53.0
-11.0	1278	945	1053	49.4	50.6
-12.0	1375	946	1056	51.6	48.4
-13.0	1470	947	1059	53.5	46.5
-14.0	1563	948	1062	55.3	44.7
-15.0	1653	950	1065	57.0	43.0
-16.0	1741	950	1068	58.5	41.5
-17.0	1827	951	1071	59.9	40.1
-18.0	1910	952	1074	61.3	38.7
-19.0	1992	953	1076	62.5	37.5
-20.0	2072	954	1079	63.7	36.3
-21.0	2150	955	1081	64.8	35.2
-22.0	2226	955	1084	65.8	34.2

4. EXPERIMENTAL STUDY

4.1 Set-up

The pressure-melting tests were carried out in a freezer. Pure degassed water is confined in a filled-up steel cylinder. The temperature and the pressure were measured in the mixture. The freezer was equipped with two heaters, each of 100 W. By using the cooling system of the freezer, the heaters and two fans a stable mixed air temperature was obtained inside the freezer. The temperature was controlled by a thermostat.

The pressure tank, a cylinder of stainless acid-proof steel, has a volume of 50 ml. During the tests the water filled steel cylinder was placed in the freezer, on a shaking-table to avoid temperature layering in the mixture. The size and shape of the steel cylinder are given in Figure 1. The temperature sensor (PT-100) is mounted through the left lid. The temperature is measured 25 mm into the ice-water mixture. The accuracy is ±0.02 ^{o}C

at 0°C and ± 0.05 $^\circ$C at -16.95°C.

The pressure gauge is mounted on the opposite lid. The piezo-electric sensor is in hydraulic contact with the mixture. Since the pressure gauge is made for temperatures above -5 $^\circ$C the electronic part of the pressure gauge is heat insulated and heated by a heat-cable. The temperature inside the insulation which is kept constant at 0°C is controlled by a thermostat. The accuracy of the pressure sensor is 0.25% which means a maximum error of 0.55 MPa = 5.5 bars.
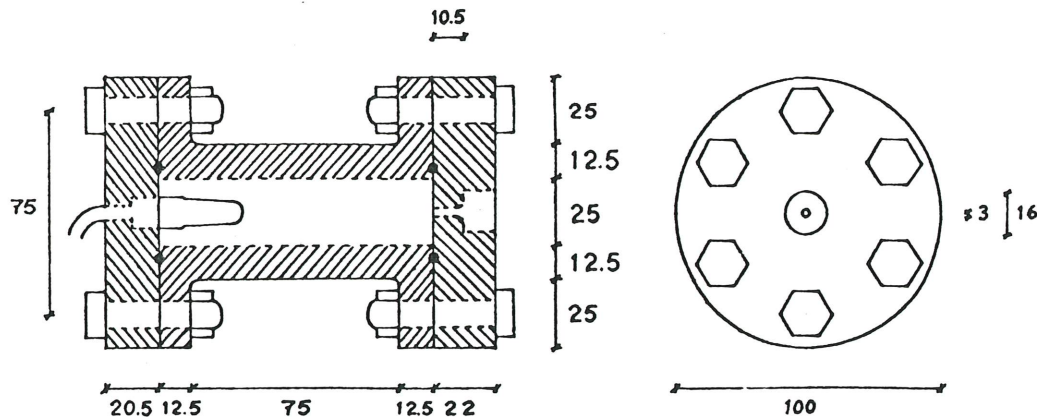
Figure 1. Section and plan drawing of the pressure-tank, of acid-proof stainless steel, used for the melting-pressure measurements at WREL. Length-scales in mm. To the left of the section the temperature gauge is seen. To the right, the hole for the piezo-electric pressure-gauge is seen. O-rings are used to tighten the lids. After Larsson (1988).

4.2 Results

The experimental data of this study are compared to the data obtained by Tammann (1903), Tammann (1910) and Bridgman (1912) in Table 2. The experimental data are also compared with the calculated melting-pressure curve, Figure 2, and found to be in good agreement. These curves also demonstrate the differences and similarities between the results of the four laboratory tests. The calculated temperature/pressure gradient is $\partial T/\partial P = -7.369 \cdot 10^{-8}$ $^\circ$C/Pa ($-7.369 \cdot 10^{-3}$ $^\circ$C/bar), between 0 and 10^4 Pa (0 - 0.1 bar). $\partial T/\partial P$ at 0°C and atmospheric pressure is many times discussed. Offenbacher (1981) suggests $-7.4 \cdot 10^{-3}$ $^\circ$C/bar.

The calculated curve, Figure 2, is closer to older measurements than it is to this study. The reason is probably that the old κ-values of Bridgman (1912) are used in the calculations.
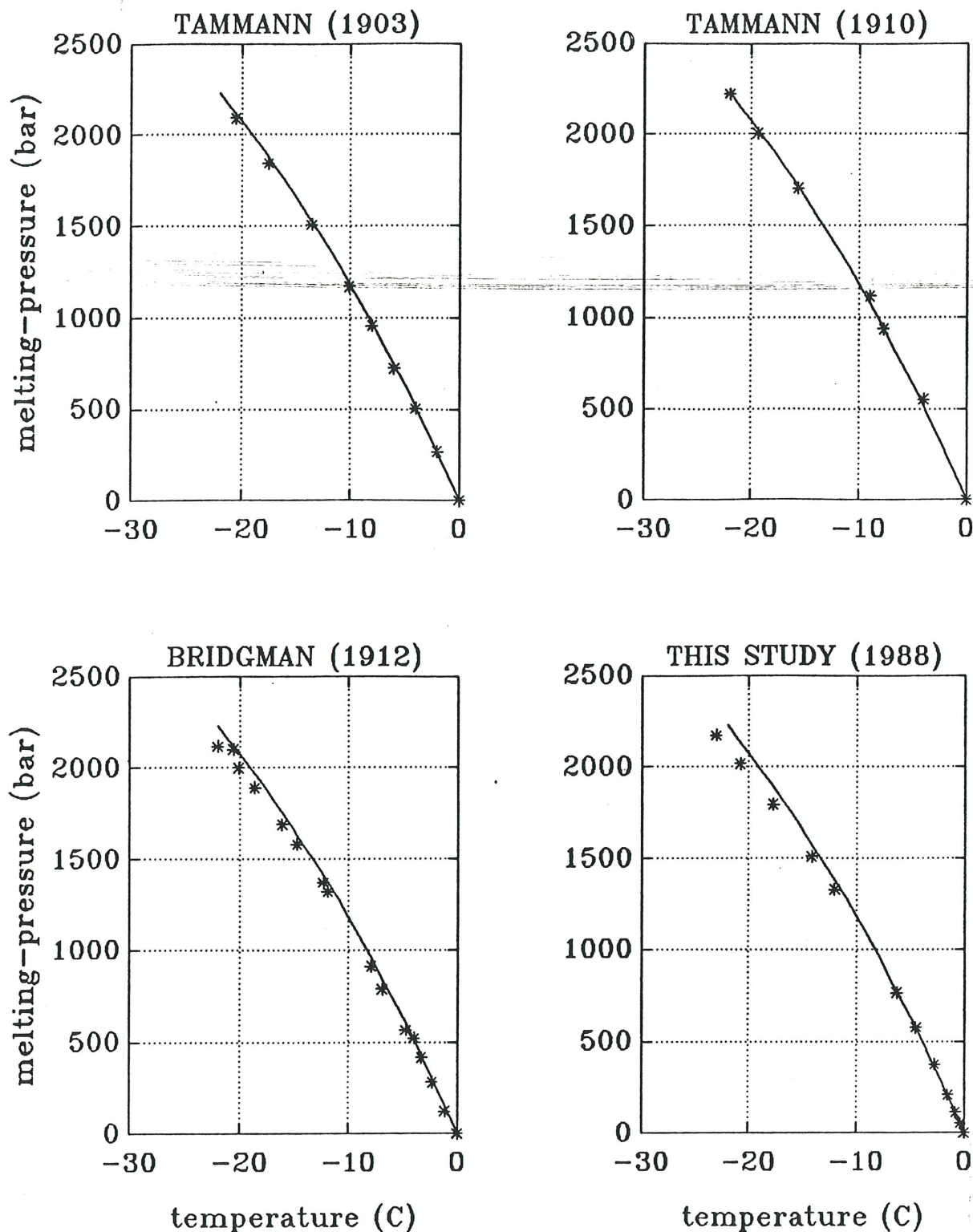
Figure 2. Measured melting-pressures of ice from Tammann (1903), Tammann (1910), Bridgman (1912) and this study (1988). The drawn curve, in all the diagrams, is the calculated melting-pressure. Calculated data of this curve are listed in Table 1.

As a consequence of subcooling pressures lower than 575 bars (>-4.5 °C), see Table 2, were measured during the melting phase. Subcooling of ice III probably occurs below -22°C since the expected maximum pressure was not obtained.

The accuracy of the performed melting-pressure mesurements is slightly improved since Tammann (1903). Tammann gives the accuracy of ±10 bars for the pressure measurements and ±0.1 °C for the temperature. In this study the corresponding values are ±5.5 bars and ±(0.02 to 0.05)°C respectively.

TABLE 2. Measured melting-pressure of ice. After Tammann (1903), Tammann (1910), Bridgman (1912) and this study (1988).

Tammann (1903)		Tammann (1910)		Bridgman (1912)		This study		
(°C)	(bar)	(°C)	(bar)	(°C)	(bar)	(°C)		(bar)
-2.00	268	-4.0	550	0	1	-0.33	m	51
-4.00	504	-7.7	935	-1.1	122	-0.78	m	112
-5.98	720	-9.0	1115	-2.3	281	-1.50	m	208
-7.98	955	-15.7	1705	-3.3	416	-2.75	m	374
-10.11	1171	-19.4	2004	-4.0	520	-4.50	f	575
-13.62	1506	-22.0	2220	-4.75	565	-6.23	f	764
-17.60	1843			-6.9	788	-12.06	f	1328
-20.56	2090			-7.9	910	-14.17	f	1510
				-12.0	1320	-17.77	f	1795
				-12.40	1370	-20.80	f	2017
				-14.80	1580	-23.12	f	2171
				-16.15	1690			
				-18.7	1890			
				-20.15	2000	m=melting		
				-20.6	2100	f=freezing		
				-22.0	2115			

5. DISCUSSION OF RESULTS

As a mental experiment, what happens if a sudden volume decrease of the total volume (ice+water) occurs?. See Table 1 and assume that the initial conditions are -5°C and and 632 bars, i.e. phase equilibrium. The volume change causes a pressure increase, assume up to 747 bars. The temperature of the ice-water mixture is still -5 °C and thus the phases are not at equilibrium. The melting point of the ice is -6°C and thus the ice starts to melt. Consequently the pressure falls until phase equilibrium is reached at 632 bars.

This mental experiment implies that a minor volume change of the total volume does not change the melting-pressure at phase equilibrium. This is of importance since the volume of the pressure tank is slightly changing during the test. There is a thermal volume change of the pressure tank and there is also a volume change depending on pressure change. These changes are opposite to each other since the pressure increases when the water temperature is lowered.

6. CONCLUSIONS

The melting-pressure of ice has been measured in a laboratory test. In earlier measurements an external pressure was used to find the melting-pressure of a small volume of ice at constant temperature. In this study the method used was quite different in principal. Water is confined in a filled up steel-cylinder which is subjected to cooling. The ice formed results in a pressure increase. At phase equilibrium the temperature and the corresponding pressure are measured.

Measured data are in good agreement with earlier measurements by Tammann and Bridgman. The method used, which is easy to handle even with this prototype equipment, should be more accurate than the old method since one possible source of error (the external pressure) is eliminated. The method could be used for other substances than pure water.

The melting-pressure calculations are based on old measurements of κ. This value is taken from Bridgman as he gives κ for both ice and water along the curve which means that they are linked to each other. A small difference of one of the κ-values result in a large deviation from the presented curve.

7. ACKNOWLEDGMENT

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