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(9) FINAL REPORT.

(6) Investigation of the Thermodynamics of Supercooled
Water and Supercooled Saline Water.

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I. INTRODUCTION

a. IMPORTANCE TO THE NAVY.

An understanding of the nature of supercooled water is very
important for understanding the thermodynamics of clouds and hence for
weather forecasting and weather modification[1,2,3]. Water in its supercooled
form is common in clouds; in fact, supercooled liquid water is more
common than is supersaturated water vapor. In his book on cloud physics,
Rogers[4] says, "...water droplets in supercooled form are the regular
state of affairs [in clouds]. Supercoolings of up to 15°C or more are
not uncommon...". This supercooled water is then nucleated to form snow
or rain. That is, rain can be formed as the nucleated ice falls into
warmer regions of the atmosphere. Some authorities[5] feel that almost
all large raindrops originate as snow or hail, and hence they can have
their origin in supercooled water. Hail is formed when frozen water
droplets accrete new layers by passing through zones of supercooled
aerosols. The freezing of the supercooled water releases heat, which
affects the temperature and turbulence of the clouds, and also causes
fragmentation of the hail. The vapor pressure of supercooled water is
needed for calculations of the nucleation and growth of water and ice
droplets in the atmosphere[6]. The vapor pressure can be used to calculate
the latent heat, which is valuable in modeling weather formations.

The supercooling of aqueous salt solutions is of importance because
there have been claims that supercooling occurs in ocean waters[7].
Thermodynamic anomalies in sea water can affect the transition of acoustic
signals through the ocean. Attenuation of sound has been observed[8] in
polar sea water and postulated to be related to ice-like fluctuations in
the water. Since sea salt is carried into the atmosphere, supercooled
salt water should also be of importance in cloud physics. Finally, an

understanding of the structure of supercooled salt solutions will be of
value in cryobiology - the science of the reaction of plant and animal
systems to extreme cold.

b. <u>RECENT DEVELOPMENTS IN THE THERMODYNAMICS OF SUPERCOOLED WATER.</u>

In the last few years much interest has developed in the seemingly
anomalous behavior of supercooled water as the temperature approaches
-45°C. The density[9,10], the isothermal compressibility[11], the specific
heat [10,12,13], and other thermodynamic quantities[14] show dramatic changes
as a "transition temperature" at -45°C is approached. The reason for
the anomalous behavior is not yet known. A number of theories have been
advanced; even the relationships between the models is not yet clear.
Rasmussen and MacKensie[10] attempted to apply a heterophase fluctuation
theory, which did not fit the data well. C.A. Angell and his collaborators[11,13]
have discussed the transition in terms of the cooperative development of
a hydrogen bond network, in terms of a cooperative change in hydrogen
bond angle, and in terms of the limit of mechanical stability for the
supercooled liquid. These hypotheses involving some sort of cooperative
phase transition have led[11,14] to the expression of the anomalous thermodynamic
properties in terms of "critical exponents" in analogy to the exponents
used to describe anomalous behavior at critical points[15]. Table I (from
Rouch <u>et al.</u>[14]) catalogs the measurements made so far and the critical
exponents describing the behavior.

We have proposed to contribute to the elucidation of the phase
change in supercooled water by measuring the vapor pressure of supercooled
H_2O, D_2O, and aqueous salt solutions. The vapor pressure data will
permit a more accurate test of Rasmussen's fluctuation theory[10] and will
allow us to test the assertion by Speedy and Angell[11] that, unlike the case of

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critical points, the specific heat at constant volume C_v shows no

divergence at all for supercooled water. That is, the relations[15]

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

Table I.[a] Behavior of some physical properties of water in the liquid and supercooled liquid domain. $\epsilon \quad (T-T_s)/T_s$ with $T_s = 228°K$.

Property	Equation	Range (°C)
Isothermal compressibility	$K_T \times 10^6 (bar^{-1}) = 29.65 \times \epsilon^{-0.349}$	-26, +10
Density	$\rho(g\ cm^{-3}) = 1.0497 \times \epsilon^{0.0243}$	-34, -23
Shear viscosity	$\eta(cP) = 1.6669 \times \epsilon^{-1.476}$	-24, 0
Diffusion coefficient	$D \times 10^5 (cm^2 sec^{-1}) = 10.34 \times \epsilon^{1.454}$	-31, -9
Sound velocity	$V(m\ sec^{-1}) = 1782.4 \times \epsilon^{0.1523}$	-10, +40
Sound absorption	$(\alpha/f^2) \times 10^{17} (sec^2 cm^{-1}) = 2.4484 \times \epsilon^{-1.7882}$	-10, +40
Ratio of specific heats	$\gamma = 0.6121 \times \epsilon^{-0.2619}$	-38, -8
Ratio of the shear to the bulk viscosity	$\eta_B/\eta_S = 0.6356 \times \epsilon^{-0.6776}$	-10, +40

[a]This table is taken from Ref. 14. The sources of all the data are given in that paper.

and [16,17]

$$\rho \frac{C_v}{T} = -\rho \left(\frac{\partial^2 \mu}{\partial T^2}\right)_\rho + \left(\frac{\partial^2 p}{\partial T^2}\right)_\rho$$

(where C_p is the heat capacity at constant pressure, ρ is the density, T is the temperature, P is the pressure, and μ is the chemical potential) can be used to relate other data on supercooled water and test for consistency.

II. PROPOSED RESEARCH PROGRAM

a. Review of previous work

·The published measurements and correlations of the vapor
pressure of supercooled water are given in Table II[18]. The earlier
measurements (1847-1891) were reviewed by Scheel in 1903[19], who found
disagreements of about 5%. He resolved the discrepancies by adding a
constant to each set of measurements so as to give a value at 0°C in
agreement with his own measurement at 0°C. Such a correction assumed
that the major source of error was in the state of the temperature scale
in the 19th century and that the ice point was comparatively easy to realize.
He then claimed agreement of about 0.3 - 1.0%, which is about the same
as the agreement of the older data with the 1909 measurements of Scheel
and Heuse[23]. The value obtained by Scheel and Heuse at 0°C agrees with
the recent measurement at the triple point at NBS by Guildner, Edsinger,
and Jones[25] to within 0.12%. On the other hand, the value of Scheel and
Heuse at -2.5° agrees with that of Douslin[24] to only 0.5%. The data at
low temperatures must be assumed to be still less accurate because of
the uncertainties in the temperature scale in the period 1847-1909.

Various workers have fitted data (mainly that of Scheel and Heuse)
to model equations [26-29]. These correlations are obviously in need of
reconsideration and revision.

We see, therefore, that the last published, extensive measurements
of the vapor pressure of supercooled water were made in 1909, that those
measurements extended only to -16°C, and that the uncertainties in the
temperature scale at that time case doubt on the reliability of those
data. We conclude that there is a need for new, precise measurements,
on the International Practical Temperature Scale of·1968 and at temperatures
approaching the nomogenous nucleation temperature (-45°C). The data so

obtained can then be used to determine new correlations of the vapor pressure.

We have found no prior work on the vapor pressure of supercooled saline water.

b. Vapor pressure program

We propose to measure the vapor pressure of supercooled H_2O, D_2O and H_2O + salt to as low temperatures as possible. We expect to measure the temperature on IPTS-68 to 0.001 K and the pressure to a precision of about 10^{-7} atm (0.01 Pa or 0.0001 Torr).

We are measuring the pressure with transducers using tunnel diode oscillators (TDO). This sensor, recently developed by C.T. Van Degrift[30-32], uses a diaphragm as part of the capacitor in a tunnel diode oscillator circuit. If the diaphragm is pushed upon by a gas, the pressure is sensed as a change in oscillator frequency. The TDO will be calibrated with respect to the established pressure and temperature scales. The TDO is particularly well-suited for this investigation because it can be made to utilize a very small sample; a small sample is crucial for maximum supercooling and minimum equilibration time. In addition, the TDO is made entirely of one material, which simplifies construction and materials problems and improves thermal homogeneity.

There are a number of experimental problems peculiar to the supercooled water. First, the water must be clean and in small quantity to achieve supercooling[33]. Water in a 1 cm^3 quantity can be supercooled to about -20°C. To achieve more supercooling, the water is either held in fine capillaries[11] or emulsified[10] in an inert support medium. We will work with bulk water as far as possible, achieving small sample size by having a "dew" of small water droplets in our sample cell. The material

Table II

VAPOR PRESSURE OF SUPERCOOLED WATER

Author	Range	Precision	Comments
V. Regnault[20], 1847	-30°	0.001 mm	H_2O; Residual air, ice present?
Fischer[21], 1881	-10°	0.01 mm	H_2O; 3 points
Juhlin[22], 1891	-13°	0.001 mm	H_2O
Scheel and Heuse[23], 1909	-16°	0.001 mm	H_2O
Douslin[24], 1971	-2.5°	0.001 mm	H_2O; 1 point
Bottomley[19]	-14°	0.001 mm	Unpublished; H_2O and D_2O
Proposed here	-35°	0.0001 mm	Bulk and emulsion, H_2O and D_2O

Author	Data Base	Comments
Washburn[26], 1924	Scheel and Heuse	Calcd from ice vapor pressure
Harrison[27], 1934	Extension of Washburn	
Goff and Gratch[28], 1946	Scheel and Heuse	
McDonald[25], 1965	Extension of Goff-Gratch	

o' the cell may also affect the nucleation probability and it may be necessary to try several materials.

III. PROGRESS IN THE FIRST YEAR

Coworkers on the project have been S.C. Greer, C.T. Van Degrift, and W.T. Angel. Dr. Van Degrift of the Temperature Division, NBS, and Dr. Greer, now of the Department of Chemistry at the University of Maryland, will be continuing their collaboration under a new contract to the University of Maryland (NR#051-701, contract #N001479C008).

The accomplishments of the first year have been:

1.) Thermostat assembly,

2.) Transducer construction,

3.) Sample filling system construction

4.) Initial P-T runs.

The thermostat, including 2 evacuated copper cans and an external bath for dry ice + ethanol, was assembled and instrumented with thermocouples and thermometers and provisions for the high frequency transducer leads. The thermostat instrumentation was connected through appropriate A/D converters to a minicomputer, allowing for automatic data acquisition.

Very pure water was obtained by purchasing a water triple point cell. The water from this cell was thoroughly degassed. The pressure cell was evacuated a room temperature, then opened to the water at its vapor pressure and pinched closed. Thus, on cooling, the water vapor should have condensed into a fine "dew" in the cell.

The TDO cell itself was made of silver and cleaned in a ultrasonic cleaner before filling.

Unfortunately, this first TDO cell has a temperature sensitivity which is so large as to interfere with our vapor pressure measurements. This temperature dependence can be due to improper annealing of the diaphragm or to a mechanical imperfection in the diaphragm.

We made four runs using this "faulty" transducer and were able to get some useful information with it. In the first place, we were able to cool the liquid water to about -20°C each time. This is encouraging and we hope to do even better by giving some attention to filtering and to preparation of the metallic surface. Although most of our data contain too much temperature dependence to be of value, we were able to extract values for the difference in vapor pressure between supercooled water and ice at the points where our samples froze. These points (near -20°C) are consistent with Bottomley's data[18] at temperature greater than -15°C and are about 10% lower than would be expected from the Smithsonian Meteorological Tables[36].

We have near completion 3 new transducers in which we hope to minimize the temperature sensitivity and maximize the pressure sensitivity. These new measurements will be made under the new contract at the University of Maryland (NR#051-701, contract #N001479C008). The thermostat is on loan to Dr. Greer at the University and University funds have been used to obtain the necessary electronics for the data acquisition.

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