Vapor Pressure Measurement of Supercooled Water

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ABSTRACT

A new dewpoint hygrometer was developed for subfreezing temperature application. Vapor pressure of supercooled water was determined by measuring temperatures at the dew-forming surface and the vapor source ice under the flux density balance, and by application of measured vapor pressure over ice from the Smithsonian Meteorological Table.

The measured vapor pressure of supercooled water agreed well with the tables above approximately $-20^\circ$C, but below that temperature, a significant lowering of the pressure was discovered. An empirical equation to best fit the measured data was obtained. At $-30^\circ$C, the estimated specific latent heat of condensation became slightly higher than the table value by $3.4\%$, that of fusion considerably lower by as much as $66\%$, and the specific heat of supercooled water amounted to as much as $3.7$ cal g$^{-1}$C$^{-1}$.

Possible implications of the new results are pointed out. For example, the latent heat associated with cloud glaciation at temperatures colder than $-20^\circ$C, and especially colder than $-30^\circ$C, is found to be less than previously thought.

1. Introduction

Vapor pressure of supercooled water is one of the most fundamental properties required when the liquid phase of water substance is studied under subfreezing temperatures, such as microphysical processes of clouds at high altitudes or low temperatures. The best data currently available for the saturation vapor pressure are those listed in the Smithsonian Meteorological Table or the International Meteorological Table, mostly due to Goff (1942, 1949) and Goff and Gratch (1945, 1946), and are based on measurements between $0^\circ$ and $100^\circ$C. There exists no completely satisfactory formula for the vapor pressure over liquid water at a temperature below $0^\circ$C (List 1966), and data in the tables are indeed direct extrapolation from the above range. Studies of supercooled water in emulsion form (Rasmussen and MacKenzie 1973; Angell et al. 1982) indicated a sharp increase in the specific heat as the temperature lowers toward $-40^\circ$C. A need for reliable measurement of the vapor pressure of supercooled water was mentioned in Pruppacher and Klett (1978). To carry out such a measurement, use of a process that directly involves the vapor phase is preferable. Devising such a new, direct method of measurement, we have recently been able to determine the vapor pressure of the unstable phase of water (Gramada 1998) and report the result below.

2. Method of measurement

To accurately measure the vapor pressure of deeply supercooled water, it is essential to use a phenomenon in which the vapor is directly involved and to assess the pressure from that, instead of relying on an indirect technique that determines relevant thermodynamic properties. In the indirect method, holding the supercooled condition for any length of time tends to disrupt the condition of the system because of the onset of ice nucleation. The dewpoint hygrometer method avoids this problem. The measurement ends at the moment of vapor condensation and requires no time for holding the condensed liquid phase in a supercooled state, since the process for water substance obeys the Ostwald Law of Stages (Dufour and Defay 1963) or the vapor condenses into the form of liquid first, instead of solid at temperatures above approximately $-38.5^\circ$C. As described below, the well-recognized stage is indeed confirmed on the dew condensation surface of the hygrometer, operated continuously down to the limiting temperature where the observed condensed phase showed a spontaneous change. Since the unstable phase leads to such a change and water is the only unstable condensed phase under the condition of measurement, the observed condensed phase proves to be water under the condition of supercooling.

The dewpoint hygrometer method requires a well-defined reference vapor source with high reproducibility. To this end, saturated vapor over ice is selected since it has the equilibrium property of the stable phase, and...
the specific latent heat of deposition $L_d$ is virtually constant. Thus, the tabulated values are reliable being based on measurement. Saturation vapor pressure is a sole function of temperature $T$ so that slow variation of temperature yields the necessary change of vapor pressure. At the moment of dew-forming nucleation, the effect of temperature difference at the source can be estimated by the flux density balance as will be shown below.

**a. Design of apparatus**

The design of the dewpoint hygrometer used in the present study is shown in Fig. 1. It is made of two copper blocks. The top block has ice holes as well as adjacent grooves for thermocouples. A coil of copper tubing is used for cooling liquid from a refrigerated, circulating bath. The bottom block is attached to a thermoelectric unit that is cooled by the same cooling liquid and has a thermocouple hole leading to the polished observation surface. Both are separated by a thermally insulating Plexiglas cylinder, and all of them are O-ring sealed so that they can be separated for service. Copper–constantan thermocouples are embedded in grooves with a thermal compound. A slide projector is used to illuminate the observation surface (upper horizontal surface of lower block) through the Plexiglas wall, and detection of condensation onset was carried out from above by a stereomicroscope with a rubber sleeve insulating the top of the upper copper block and the lens from the surrounding room air. The whole apparatus is thermally insulated by polypropylene foam.

**b. Measurement**

In preparation for measurement, ice holes at the lower surface of the top copper block are filled with distilled water. Then, the whole system is chilled by cooling liquid from the refrigerated, circulating bath to a temperature slightly above that on the observation surface. For operation at temperatures close to the melting point of ice, the system is first chilled to a sufficiently low temperature to freeze the water in the ice holes. It is then allowed to warm up to the temperature of measurement. When the temperature has stabilized and the water in the ice holes is frozen, the electric current to the thermoelectric unit is slowly raised while the polished surface of the (cooling) bottom copper block is being observed by the microscope. At the moment the dewpoint condensation occurs, the surface appearance suddenly changes, and the temperatures of the top and bottom blocks are recorded with a time mark on a strip chart recorder. Then, polarity of the current to the thermoelectric unit is reversed to warm the bottom block surface to evaporate the condensed water. The temperature at which the condensed water has completely evaporated is also recorded. By recovering the original polarity of the current and after quickly coming close to the condensation point previously assessed, a new but reduced cooling rate is applied, and the temperature of condensation is redetermined with higher accuracy.

The above procedure of measurement was repeated with the whole system incrementally warmed from a low temperature or cooled from a high temperature.

**3. Result of measurement and discussion**

**a. Balance of vapor flux densities**

At the moment of condensation, the water vapor flux density from ice in the top copper block at higher temperature $T_i$ balances with that of water drops on the bottom copper block at lower temperature $T_w$ or

$$n_iu_i = n_wu_w,$$  

(1)

where $n$ and $u$ are the number density and velocity of water molecules in the normal direction, and subscripts $i$ and $w$ stand for ice and water, respectively. The gas kinetics shows

$$T \propto u^2,$$  

(2)

and the ideal gas law combines these properties with the vapor pressure as

$$e \propto nT.$$  

(3)

From relationships (1), (2), and (3), we have

$$\frac{e_w}{\sqrt{T_w}} = \frac{e_i}{\sqrt{T_i}},$$  

(4)
where \( e'_i \) is the saturation vapor pressure over ice at temperature \( T_i \) of the top block. By measuring \( T_w \), the temperature of the bottom block at the moment of dew formation, and \( T_i \) and using \( e'_i(T_i) \) in the table, one can determine \( e_w \) at \( T_w \). In the treatment, the Kelvin effect of the vapor pressure increase above the saturation is ignored. This approximation is validated by the close match of the data between the measurements and the table value in the slightly supercooled zone.

**b. Thermodynamic properties**

The Clausius–Clapeyron equation in the integral form gives

\[
\ln \frac{e}{e_i} = \frac{L}{R_e} \left( \frac{1}{T} - \frac{1}{T_i} \right),
\]

where \( e \) is the vapor pressure of the condensed phase at \( T \), \( e_i \) is the same at \( T_i \), \( L \) the average specific latent heat of phase change over the temperature range between \( T \) and \( T_i \), \( R_e \) is the specific gas constant for water vapor, and \( T_i = 273.15 \) K under 1 atm, which stays within 0.01 K at the atmospheric pressure of the present measurement 0.85 atm.

Applying Eq. (5) to water and ice in equilibrium with the vapor

\[
\bar{L}_f = R_e \ln \left( \frac{e}{e_i} \right) \left( \frac{1}{T} - \frac{1}{T_i} \right),
\]

where \( \bar{L}_f \) is the average specific latent heat of fusion over the temperature range between \( T \) and \( T_i \), \( e_w \) and \( e_i \) being saturation vapor pressure over water and that over ice under the same temperature \( T \), and

\[
\bar{L}_f = \frac{L_f + L_i(T_i)}{2}.
\]

In Eq. (7), \( L_f \), the specific latent heat of fusion at \( T_i \), may be calculated based on \( L_i(T_i) \) from the table and \( \bar{L}_f \) from Eq. (6) in which \( e_w \) is determined experimentally based on \( T_w \) and \( T_i \) measurements in Eq. (4).

Among the specific latent heats of phase change, the thermodynamic relationships are

\[
L_f = L_d - L_c,
\]

where \( L_d \) and \( L_c \) are and the specific latent heat of deposition and that of condensation, respectively, and

\[
\bar{L}_f = \bar{L}_d - \bar{L}_c.
\]

In addition, the Kirchhoff equation gives

\[
c_{p,w} - c_{p,i} = \frac{dL_f}{dT},
\]

where \( c_{p,w} \) and \( c_{p,i} \) are the specific heat at constant pressure for water and ice, respectively.

Figure 2 shows the vapor pressure ratio between the observed and the table values for supercooled water. As can be seen in the figure, there is no appreciable difference for datasets when the hygrometer operation was repeated with whole system cooled (cooling) stepwise from a high temperature or warmed (warming) from a low temperature. On the other hand, datasets for droplet evaporation are clearly lower. This is because, at the time evaporation measurements were to begin, droplets already had achieved some size due to condensational growth at the dewpoint. To observe the relative change of the droplet size under the condition, a slightly larger vapor pressure difference was needed, which lowered the measured vapor pressure of water. For this reason, more weight was put on condensation data when the representing curve was drawn. At the moment of condensation, droplets start growing practically from zero size and the process is very sharp. The good agreement between the two values in the temperature range down to about \(-20^\circ C\) also supports the accuracy of the present measurement.

When the temperature of the observation surface was lowered toward the dewpoint, while holding the temperature of the vapor source ice in the upper copper block constant, the corresponding vapor pressure ratio in Fig. 2 moves downward from above. A slight delay of dewpoint detection tends to place the observed point below the exact dewpoint value. This tendency is clearly visible above approximately \(-20^\circ C\) with the upper limit of data on the line drawn from the table values. For this reason, a curve representing the measured data was drawn close to the top of them, consistent with the relationship above approximately \(-20^\circ C\).
thereafter (Fig. 2). The measured values around $-36^\circ$C or lower contain a large amount of error due to the homogeneous freezing process, which quickly follows the condensation.

An empirical equation of polynomial form for the curve drawn in the figure is obtained as

$$
e_{M}/e_{T} = 0.9992 + 7.113 \times 10^{-4}x - 1.847 \times 10^{-4}x^2$$

$$+ 1.189 \times 10^{-3}x^3 + 1.30 \times 10^{-2}x^4$$

$$- 1.743 \times 10^{-5}x^5,$$

(11)

where subscripts $M$ and $T$ stand for “measured” and “table,” $x = t + 19$, and $t$ is the temperature in degrees Celsius. The deviation of Eq. (11) from the plotted curve is within 0.2%.

The thermodynamic properties of supercooled water thus determined are listed for the temperature range below $-20^\circ$C in Table 1, where subscripts $M$ and $T$ are as given in Eq. (11). The largest deviation from the table value is seen with the $L_v$ ratio in the fifth column. The ratio decreases from 0.962 to 0.404 as the temperature drops from $-20^\circ$C to $-35^\circ$C. For the same temperature change, the ratio between the observed and table values shifts from 0.977 to 0.917 for the vapor pressure of supercooled water, and from 1.004 to 1.065 for the specific latent heat of condensation.

Figure 3 shows the ratio of specific latent heat of fusion between the measured and the table values. Like the deviation of measured vapor pressure from the table value shown in Fig. 2, the observed latent heat of fusion begins to come down as the temperature lowers and appears to asymptotically approach zero at some temperature below $-40^\circ$C.

The value of $c_{pw}$ was determined at $-30^\circ$C from Eq. (10) with $c_{ps} = 0.45$ cal g$^{-1}$ °C$^{-1}$ and found to be 3.7 cal g$^{-1}$ °C$^{-1}$, 3.4 times larger than that measured in the emulsion cooling method (Rasmussen and Mackenzie 1973; Angell et al. 1982). Water-in-oil emulsion used in their studies isolates freezing events of droplets and avoids glaciation of the whole system. Nonetheless, the latter method is influenced by the solubility of the carrier oil in water, the necessarily high cooling rate (on the order of 10 K min$^{-1}$ for the system consisting of mostly oil with small thermal conductivity), and the problem of emulsified water freezing under prolonged condition of supercooling.

The reason for the sudden appearance of the deviation in the measured saturation vapor pressure at around $-20^\circ$C is not clear at this moment, but since hydrogen bonding is known to be attributed to many unusual behaviors of water substance in the condensed phases, we hypothesize that a new mode of bonding is starting at the temperature. Nevertheless, the discovery that the behavior of saturation vapor pressure deviates significantly from values extrapolated from higher temperatures indicates that special attention must be given to the temperature zone of the unstable phase.

The discrepancy found at temperatures below $-20^\circ$C between the measured data and table values is expected to shift the current view in the following atmospheric processes, especially below $-20^\circ$C. The vapor pressure decrease in the case of supercooled water will lead to a slightly lower cloud-base altitude than that assessed by the existing table values and larger liquid water content there.

Cloud glaciation will lead to considerably weaker heating and the associated buoyancy development than those previously assessed (Fukuta 1973), while cloud formation results in more heating due to the increased $L_v$. The largest impact is anticipated with the mechanism of homogeneous freezing nucleation (Pruppacher 1995).

In the nucleation process, the surface free energy at the water–ice interface is involved, and if Antonov’s rule of proportionality between the surface free energy and the corresponding specific latent heat applies, the observed large deviation in the specific heat of fusion from the table value previously used is expected to change the corresponding surface free energy significantly and, therefore, the nucleation rate. The observed data of vapor pressure also provide an accurate foundation to assess physicochemical properties of supercooled water.

### 4. Conclusions

A dewpoint hygrometer was developed that permits accurate measurement of saturation vapor pressure of...
supercooled water for the first time down to the temperature close to the homogeneous freezing nucleation point $-38.5^\circ C$, making use of measured saturation vapor pressure over ice in the Smithsonian Meteorological Table as a reference under the flux density balance between the ice vapor source and vapor sink on dew condensation surface.

The measured vapor pressure of supercooled water agreed well with the tables above approximately $-20^\circ C$, but below that temperature down to about $-35^\circ C$, a significant lowering of the pressure was discovered. Taking the data closest to the actual onset of dew formation, an empirical equation was obtained to best fit the measured data. At $-30^\circ C$, the estimated specific latent heat of condensation became slightly higher than the table value by 3.4%, that of fusion considerably lower by as much as 66%, and the specific heat of supercooled water amounted to as much as 3.7 cal g$^{-1}$ $^\circ C^{-1}$.

Implications of the new measurements were pointed out with respect to physicochemical properties, cloud microphysical, dynamical, and thermodynamical processes involving supercooled water and its phase change processes.

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REFERENCES