Heat of Freezing for Supercooled Water: Measurements at Atmospheric Pressure

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Supporting Information

ABSTRACT: Unlike reversible phase transitions, the amount of heat released upon freezing of a metastable supercooled liquid depends on the degree of supercooling. Although terrestrial supercooled water is ubiquitous and has implications for cloud dynamics and nucleation, measurements of its heat of freezing are scarce. We have performed calorimetric measurements of the heat released by freezing water at atmospheric pressure as a function of supercooling. Our measurements show that the heat of freezing can be considerably below one predicted from a reversible hydrostatic process. Our measurements also indicate that the state of the resulting ice is not fully specified by the final pressure and temperature; the ice is likely to be strained on a variety of scales, implying a higher vapor pressure. This would reduce the vapor gradient between supercooled water and ice in mixed phase atmospheric clouds.

INTRODUCTION

Freezing of a supercooled liquid is an irreversible process, and as a consequence, heat released in the process depends on the degree of supercooling. For example, crystallization of 1 mol of liquid water at the melting point at atmospheric pressure is accompanied by the release of 6007 J.† If, however, the water is initially supercooled by 20 °C, the latent heat of freezing is thought to decrease from the value at the melting point by at least 10%. The temperature dependence of the heat of freezing of water is important for areas as diverse as the dynamics of glaciating clouds‡ and homogeneous nucleation of ice.§ In the latter case, quantifying the heat released at a given temperature is especially important because it appears (quadratically) in the exponential term of common expressions for the nucleation rate. As an example, reducing the heat of freezing by 20% implies a reduction of the homogeneous nucleation rate from ∼10⁸ cm⁻³ s⁻¹ to 1 at −36 °C.

Although our emphasis here is on the heat of freezing for water, the methods used to acquire the data and the framework employed to interpret it are general. We find that the irreversibility inherent in a first-order phase transition originating from a metastable state (as opposed to one occurring on the phase boundary) reduces the heat exchanged between the crystallizing material and its environment. In order to highlight that irreversibility, we begin our examination of the temperature dependence of the heat of freezing with an expression that assumes reversibility; it serves as a benchmark for the measurements we present. Kirchhoff’s relation, which relates the enthalpy difference between product and reactant at constant pressure to the difference in the heat capacities is:¶

\[
\left(\frac{\partial \Delta h}{\partial T}\right)_p = \Delta c_p
\]

Integration of eq 1 leads to:

\[
L_f(T_f) = L_f(T_m) - \int_{T_f}^{T_m} [c_w - c_i] dT
\]

where we have substituted the latent heat, \(L_f\) for \(\Delta h\), \(L_f(T_m)\) is the latent heat at the melting point, \(c_w\) is the heat capacity of liquid water, and \(c_i\) is the heat capacity of ice. Note that eq 2 is defined so that a flux of heat from a droplet, for example, is positive. (See the Supporting Information for two other routes to eq 2. One is based on a physical model while the other is an extension of the triple point identity.)

Once the initial temperature is specified in eq 2, the latent heat of freezing is fixed because the heat capacities are known. However, unlike hydrostatic systems (e.g., liquid water, air), temperature and pressure do not determine the thermodynamic state of a solid; the components of the stress tensor and perhaps the concentration of defects must also be specified.‡ We have conjectured that ice resulting from deeply supercooled water is “hurriedly” made and is therefore likely to be strained on a variety of scales with a higher concentration of defects than ice in equilibrium at a given temperature and pressure.§ For freezing, the irreversibility of the process and the fact that solids are not hydrostatic are intimately related. In recognition of that fact, we refer to the “irreversible heat of freezing” or simply “heat of freezing” rather than the “latent heat of freezing.” (We reserve “latent heat” for reversible phase transitions.)

Special Issue: Victoria Buch Memorial

Received: April 14, 2010
Revised: November 3, 2010
Published: November 18, 2010
Formation of defects and establishment of stress–strain within a crystal requires energy, which may diminish the heat released during crystallization. Ice formed via rapid freezing of deeply supercooled water should bear the scars of the irreversibility of its formation. Is the heat released to its surroundings considerably diminished as well? In answer, we present calorimetric measurements of the irreversible heat of freezing of water, which show that it may be 10–20% lower than the amount released over reversible paths in which ice is treated as a hydrostatic system.

**EXPERIMENTAL METHODS**

Most of our measurements were made with a Perkin-Elmer differential scanning calorimeter (DSC) 7, which operates on the principle of power compensation. An example of a peak resulting from crystallization of a 10 μL droplet in a PS1007 hermetic sample pan (Al, Instrument Specialists, Inc.), the sample size used in all our experiments, is shown in Figure 1. The two pieces of information that we extract from the data are the temperature and corresponding heat of the phase transition.

The temperature of the phase transition is determined from the intersection of a straight line fit to the leading side of the peak with the baseline. In the case shown in the figure, \( T_{\text{freeze}} = -22.5^\circ C \). Unlike freezing, melting occurs at a well-defined temperature so the melting point temperatures that we deduce from our data can be compared with the literature values. Figure 2 is a histogram of melting temperatures of ice in the Perkin-Elmer. The mean is \( T = 2.4 \times 10^{-3} \pm 0.2 \) °C. Hence, we adopt an uncertainty in the temperatures reported here as ±0.2 °C.

The area under the curve in Figure 1 is a measure of the heat of the phase transition. We note that because we have used nonzero cooling (or heating) rates, the phase transitions, as measured, span a finite temperature range. The area under the peaks must then be corrected for cooling (or heating) of the final phase. For example, the correction to the data shown in Figure 1 is

\[ \Delta T = 35 \text{ J mol}^{-1} \text{ K}^{-1} \times 5.4 \text{ K} = 190 \text{ J mol}^{-1}, \]

where we have assumed that ice is created at the normal melting point \( T_m = 273 \) K so that all the resulting ice is cooled from the melting point to the temperature at which the baseline is reestablished.

Figure 3 shows the result of our measured temperatures and latent heats of melting for dodecane, tetradecane, undecane, and water, which span the temperature range -25 to +5 °C. All of the data fall on the 1:1 line within the uncertainty of the measurement.

**Measured Heat of Freezing.** Figure 4 is a plot of values of the heat of freezing from four groups including ours, with a plot of \( L_f \) as reference. All values on the plot are the result of calorimetric measurements except those of Fukuta and Gramada, which are derived from the difference in the vapor pressure of supercooled water and ice at the same temperature. As outlined above, \( L_f \) is
the heat of freezing that would be realized for a reversible process if the ice were hydrostatic. \( L_f \) is calculated from eq 2, using \( L_f - (T_f - T_m) \) and taking the values of the heat capacities of water and ice (\( c_p \) and \( c_i \)) from Archer and Carter\(^{14} \) and Haida et al.,\(^{1} \) respectively. Most of the measurements are significantly less than \( L_f \). The majority of the data of Bertolini et al. are approximately 10% below \( L_f \) at the deepest supercooling they achieved. Our data show almost a 20% discrepancy at 248 K, whereas those of Fukuta and Gramada are nearly a factor of 2 lower than \( L_f \) at 238 K.

Given the discrepancy between three independent, calorimetric measurements and \( L_f \), we conclude that the way in which supercooled water freezes affects the amount of heat exchanged with its surroundings. In other words, we conclude that the heat of freezing is path dependent, which also follows from the irreversibility of a phase transition initiated from a metastable state. We now proceed to examine the difference between the latent heat of fusion, which is applicable for a reversible path and for hydrostatic substances, and the irreversible heat of freezing.

**Effect of Irreversibility on the Heat of Freezing.** As motivation for the effect of irreversibility on the heat exchange between a freezing drop of water and its environment, consider the following thought experiments.

(1) A droplet of supercooled water is injected into an isobaric, isothermal chamber. The vapor pressure in the chamber is less than the droplet’s equilibrium vapor pressure. The droplet evaporates. The energy (heat) exchanged between the chamber and its environment because of the droplet’s evaporation is \(-m_dL_v\), where \( m_d \) is the mass of the droplet.

(2) A droplet of supercooled water is injected into a chamber identical to the one described in item 1. The droplet freezes, resulting in a single crystal of ice, which then sublimes. The energy (heat) required is \( m_d(L_f - L_v) = -m_dL_v \). In other words, after the heat of freezing is released to the chamber, the latent heat of sublimation is required for the crystal-to-vapor phase change.

(3) A droplet of supercooled water is injected into a chamber, identical to the ones in items 1 and 2. The droplet freezes, but the resulting ice is polycrystalline. How much heat is exchanged between chamber and droplet as the ice sublimes? Is the heat of freezing the same in this case as for the previous example?

The answer to the first question posed in item 3 must be \(-m_dL_v\) because the initial and final states are the same as in item 1. The heat of freezing, however, must be different because of the energy associated with grain boundaries; the energy is spent to create grain boundaries and is not released as heat as the water crystallizes.

As we argue above, grain boundaries or other defects (in excess of the equilibrium concentration) are the result of irreversible processes in freezing. The further the system is from stable equilibrium when the process is initiated, the more net entropy is created.\(^{16} \) An extreme example would be a small droplet of water cooled so fast that the water cannot adopt its crystalline configuration and solidifies in a glassy state. The “defects” dominate the structure to the extent that there is no crystal. Cooling rates in the atmosphere never approach such extremes, but, nevertheless, the structure of ice is a function of how deeply the initial liquid was supercooled, as measurements have shown.

Hallet\(^{17} \) found that water droplets (500—1300 μm radius) froze as single crystals for \( T \geq -5 \, ^\circ \text{C} \), but at deeper supercoolings, the droplets were polycrystalline, ranging from 5 ± 2 crystals at a supercooling of 10 °C to 300 ± 100 at \(-30 \, ^\circ \text{C} \). Electron microscopy of frozen droplets of a sucrose solution reveals structural differences within the droplet,\(^{18} \) corresponding to the region of rapid growth upon nucleation and the region where growth is limited by heat transfer. The region of rapid growth is characterized by a fine grained appearance, whereas the surrounding material where the growth of the ice was limited by heat transfer was coarser and had a more dendritic appearance. Previous work on spray frozen water had shown crystallites with dimensions on the order of 20 nm.\(^{19} \)

Does this difference in structure affect the heat exchange between freezing water and its surroundings? Bertolini et al.\(^{1} \) state that their aim in measuring the heat of freezing was to invert the data, using eq 2, to obtain the heat capacity of deeply supercooled water. Confronted with data that systematically fell below the values predicted by eq 2, they wrote: “After detailed consideration of the experimental apparatus and procedure to eliminate possible artifacts, we conclude that our data support the existence of a transient solid phase (or phases) in the ice just grown from the liquid phase.” After a similar consideration of the experimental evidence, our hypothesis is that the transient solid phase to which Bertolini et al. refer is defect-riddled ice and that the energy associated with grain boundaries and defects (extended and point) reduces the heat of freezing.

The question then becomes whether the energy associated with these effects suffices to explain the differences apparent in Figure 4. As one example, the energy per area associated with grain boundaries in ice is \( \sim 50 \, \text{mJ m}^{-2} \).\(^{12} \) For 10 μL, the volume of water used in our experiments, the heat of freezing is \( \sim 3 \, \text{J} \). If our droplets froze as polycrystalline ice with a grain boundary area of 6 m², approximately 0.3 J would be associated with the grain boundaries and not released as part of the heat of freezing. Such an internal surface area would correspond to individual grains of 10 nm in diameter, which is small but not inconceivable. Calorimetric studies have shown that up to 30% of the latent heat of freezing is associated with grain boundaries.

Figure 4. Measured values of the heat of freezing from Clausse et al.,\(^{11} \) Fukuta and Gramada,\(^{12} \) Bertolini et al.,\(^{1} \) and our measurements, plotted with \( L_f \) as a reference. The points labeled “isothermal” were acquired by ramping the sample to a specific temperature, then waiting for it to freeze. (The initial and final temperature are the same.) The freezing events labeled “ramped” were acquired as the temperature was decreasing at rates ranging from 20 to 1 °C/min.
of fusion can be associated with grain boundaries in nanocrystalline selenium (grain sizes ranged from nine to 22 nm). The presence of grain boundaries in polycrystalline material has also been shown to affect the heat capacity.

All the energy not released as heat may not be associated with grain boundaries within the material. There are other mechanisms that would also trap energy within the ice. For example, energy is required for the formation of point defects. The cost to form an interstitial in ice is 0.4 eV. In a 10 μL drop, 4.7 × 10^18 interstitials would reduce the heat of freezing by ~10%, which corresponds to roughly 1 in 100 molecules as an interstitial, compared to 1 in 10^6 for ice in equilibrium at 0 °C.

**Interpretation of the Measurements.** The two examples just outlined provide plausible mechanisms for how the heat of freezing might be reduced in an irreversible process. However, even a cursory examination of Figure 4 shows that not only does the data fall below L_0 but that the data from one group does not agree with data from others. (Also note that there is substantial scatter in data from a single group.) The differences among groups can, perhaps, be explained by the differences in the measurement conditions. For instance, the difference between our data acquired with the Perkin-Elmer and that of Bertolini et al. can be explained by the differences between the two calorimeters. Both measurements must result in ice that is strained and/or defect-rich, but the fact that our measurements fall farther below L_0 than do those of Bertolini et al. indicates that our measurements are, in some sense, more irreversible than theirs. The Perkin-Elmer is a power compensated calorimeter. The temperature difference between the sample and reference pans is monitored and the power to the sample pan is adjusted to force the equality T_sample = T_reference. It is that adjustment in power to the sample pan that is reported by the instrument.

As a consequence of the feedback loop just described, strong temperature gradients must develop in a freezing water sample in the Perkin-Elmer. Ice in contact with the bottom of the pan will be close to the programmed temperature (~ the freezing temperature shown in Figure 4), while the ice-water interface will be at the normal melting point, resulting in gradients approaching 25 °C mm^-1. The calorimeter that Bertolini et al. used was custom built.

In essence, it derives the heat flux from the sample by measuring the temperature difference between sample and reference cells as a function of time. They report a typical increase in the temperature of the sample cell of 1 °C. In other words, for a given freezing temperature, the gradients are not as steep in their apparatus because the heat of freezing is not dissipated as quickly. In fact, to test that very assumption, Bertolini et al. insulated two of their samples by enclosing the water in another capillary tube, thus reducing the heat transfer out of the water even further. Those two points, at ~248 K, exceed L_0. Bertolini et al. attribute the difference between samples which were well-coupled to the thermal bath of the calorimeter and those which were insulated to the fact that... the ice sample explores temperatures much higher than T_mf.

This is also consistent with the difference between our data and theirs. The power compensation DSC removes heat from the freezing water almost as soon as it is released, whereas their apparatus allows the heat to warm the sample, even if by 1 °C.

As further support for this line of reasoning, consider the points labeled "this measurement, Mettler Toledo" in Figure 4. As indicated, that data was acquired with a Mettler Toledo DSC, which operates on the heat flux principle. The values exceed L_0 which cannot be explained by ice which has a higher entropy because it was frozen quickly. As explained above, a freezing process that resulted in ice like that would have exchanged less heat with its surroundings, not more. How can the heat of freezing exceed L_0?

The answer can be discerned from Figure 5, which shows the temperature of sample and reference for a measurement with the Mettler Toledo. Upon freezing, the measured temperature of the sample increases by more than 5 °C. The rise in temperature is quite rapid, ~3–4 s; the decay back to the baseline is also comparatively rapid, approximately 20 s. We believe that the rapidity of that decay is responsible for the fact that the values of the heat of freezing measured using the Mettler Toledo exceed L_0. The decay time must be faster than the ice's relaxation time, trapping it in a configuration consistent with the higher temperature.

Previous work has shown that the concentration of defects in ice is time and temperature dependent. A series of X-ray topographic images showed, for instance, stacking faults in freshly grown crystals (~20 °C), which annealed out after 12 days, and dislocations that were the result of rapid cooling of a crystal of ice. Warming the ice has the effect of annealing out defects, so crystals which ... probe temperatures much higher than T_mf, and are then cooled rapidly, are trapped in a state consistent with the higher temperature. (Rapid is defined here as a time scale much less than the time required for ice to equilibrate, given a sudden change in temperature.) The higher temperature is associated with a higher heat capacity, which would propagate into a higher effective irreversible heat of freezing. (eq 2 shows that L_0 increases with an increase in c_v.)

We conclude our discussion with the observation that all calculations of thermodynamic quantities rely on the existence of a reversible path connecting two states. One classic example is the calculation of the change in entropy upon free expansion of an ideal gas into a vacuum. The process is irreversible, but ΔS is easily determined because the initial and final states of the gas can be connected by an isothermal expansion. In our case, however, there may be no reversible path connecting supercooled, liquid water and “hurriedly made” ice. Imagine starting with ice, which is not at a global free energy minimum, and heating it. At some point, the defects (including grain boundaries), will begin to...
anneal out. When that occurs, reducing the temperature back to its original value does not return the ice to its original state; the path is not reversible. Apparently a path traversed solely by heating and cooling is not reversible in this case. Similar arguments show that performing work on the ice will not introduce defects and/or grain boundaries reversibly. Unlike supercooled water, which though it is in a metastable equilibrium and can be reached on a reversible path, it is not necessarily accessible via any reversible route.

**Implication for the Atmosphere.** The state of the ice, which we have highlighted in the preceding discussion, may affect the vapor pressure. The logarithm of the ratio of the vapor pressures of ice and supercooled water at a temperature \( T \) is:

\[
\ln \left( \frac{p_w}{p_i} \right) = \frac{(L_s - L_v)(T_0 - T)}{RTT_0} \tag{3}
\]

where \( L_s \) and \( L_v \) are average values of the latent heats of sublimation and vaporization, chosen to make the integration of the Clausius–Clapeyron equation from \( T \) to the melting point, \( T_0 \). Exact \( L_s - L_v \) can be identified as \( L_s - L_v \).

Equation 3 implies that a freezing event which releases less heat than \( L_f \) will result in ice that has a higher vapor pressure than ice which has had time to anneal. For mixed phase clouds, where supercooled water and ice coexist, such a difference could have profound consequences. Because the vapor pressure of supercooled water is higher than that of ice for a given temperature, there is a net flux of vapor from supercooled water to ice in mixed phase clouds, known as the Bergeron–Wegener–Findeisen process. A higher vapor pressure over ice would slow that mass transfer.

Figure 6 is a plot of the difference in vapor pressure between supercooled liquid water and ice, as derived from eq 3. For this calculation, \( L \) is the arithmetic mean and we have calculated the vapor pressure of supercooled water using the expression found in Murphy and Koop. As expected, the differences are quite small for temperatures greater than \( -15^\circ \text{C} \), commensurate with the data in Figure 4. For lower temperatures, the differences are more pronounced; in the extreme case the difference is greater than 1 Pa, which is significant when the difference in the equilibrium vapor pressures over ice and supercooled water at the same temperature are on the order of 10 Pa.

### CONCLUDING REMARKS

Our measurements of the irreversible heat of freezing of water as a function of temperature show that the heat released by freezing of supercooled water depends upon the way in which the water freezes, that is, upon the path between initial and final state. Our measurements, and almost all others, fall below the benchmark to the heat exchange, based on a reversible path between supercooled water and the resulting ice. When deeply supercooled water crystallizes, the resulting solid is likely to be strained on a variety of scales. The energy associated with grain boundaries and defects (both point and extended) are consistent with the order of magnitude reduction in the irreversible heat of freezing that we observe. Our measurements, taken together with the reversible estimate, indicate that the state of the resulting solid is poorly specified. Ice resulting from crystallization of deeply supercooled water may be in a higher free energy state than ice formed closer to the melting point or which has annealed at a higher temperature. A consequence of that higher free energy would be a higher vapor pressure, reducing the vapor gradient between supercooled water and ice in mixed phase clouds.

### ASSOCIATED CONTENT

5 Supporting Information. The Supporting Information includes a more detailed discussion of the derivation of eq 2. This material is available free of charge via the Internet at http://pubs.acs.org/.

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**ACKNOWLEDGMENT**

This work was funded by the National Science Foundation (CHE-0410007 and ATM05-54670). We appreciate assistance and advice on the calorimeters from Kelley Smith and John Williams in the Department of Chemistry at Michigan Technological University. Stimulating discussions with Raymond Shaw and critical analysis from Dan Murphy are also appreciated. We also appreciate thoughtful reading of the manuscript by Sydney Morris and by three anonymous reviewers.

### REFERENCES

(15) Bertolini et al. specifically changed the parameters in their experiment to test the effect of heat transfer. The two points at \( \sim 248 \) K that exceed \( L_2 \) are the result of that change. We discuss that experiment in the section on interpretation of the measurements.
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