1. INTRODUCTION

Entropy can be related to a definite quantity of heat in a reversible process but associating latent heat with a phase transition from a metastable state is less clear. However, freezing in the atmosphere is always initiated from a metastable state – supercooled water.

Measurements of the latent heat of fusion as a function of temperature are difficult and remain scarce. We have been able to locate only three such measurements – Fukuta and Gramada (2003), the Smithsonian Tables (1951), and Bertolini et al. (1985). In the two studies motivated by processes in Earth’s atmosphere (Fukuta and Gramada, 2003; List, 1951) the latent heat values were obtained by using measured vapor pressures, then using the Clausius-Clapeyron equation as well as the triple point identity for the latent heats of sublimation, vaporization and fusion to extract the latent heat of fusion. In other words, the latent heat measurements are not direct and involve questionable assumptions for the supercooled (metastable) domain (see Kostinski and Cantrell (2008) for details). We re-examine the measurements and suggest a lower bound on the latent liberated during freezing of an initially supercooled water droplet. We also derive a simple estimate for the heat released in the complicated process of freezing, corresponding warming of the droplet (because of the latent heat released at the ice-water interface within the droplet as it freezes), and subsequent cooling back to ambient temperatures. Finally, we estimate the contribution of the intrinsic irreversibility of freezing to the heat production.

2. A CONSTRAINT ON THE HEAT RELEASED FROM FREEZING A SUPERCOOLED WATER DROPLET

Recall that Clausius’ definition of entropy, 
\[ dS = \frac{dq}{T}, \]
implies reversibility. Since water freezing from a supercooled state is irreversible, the release of the latent heat of fusion to the atmosphere cannot be calculated simply from the latent heat released at the melting point, where the transition is reversible. Indeed, for the reversible case, the latent heat of fusion is simply \[ T \Delta S, \]
where \( T \) is the temperature at which the transition occurs and \( \Delta S \) is the difference in entropy between water and ice.

Allowing for irreversible processes, the Second law of thermodynamics can be stated as 
\[ dS_{\text{system}} \geq \frac{dq}{T}, \]
where the equality applies for a reversible process. In the case of freezing, 
\[ dS_{\text{system}} < 0 \]
(i.e. the entropy of water decreases) and \( dq < 0 \) (heat is given off). Thus, the inequality implies 
\[ |L(T)| \geq |T \Delta S|. \]
The magnitude of the latent heat released upon freezing must equal or exceed \( T \Delta S \), which is shown as the dashed line in the figure. Figure also shows that Bertolini et al.’s data are in agreement with the bound.

![Figure 1: Bounds on the latent heat of fusion released during freezing of a supercooled droplet of water along with data from Bertolini et al. (1985).](image-url)
3. A SIMPLE APPROXIMATION FOR THE LATENT HEAT RELEASED DURING FREEZING OF SUPERCOOLED WATER

Though freezing from a metastable state is not reversible, a reversible path can be constructed, linking the initial and final states. This path can then be associated with a definite quantity of heat, because it fulfills the requirement of reversibility. The reversible path connecting water at some temperature $T_i$, below the normal melting point, and ice at the same temperature proceeds along the following lines:

1. Warm the water (reversibly) to the melting point.
2. Freeze the water, releasing the latent heat of fusion. (This process is reversible because it is on the equilibrium phase boundary.)
3. Cool the resulting ice back to $T_i$.

Mathematically, the path can be written as:

$$L'(T_i) = L_m - \int_{T_i}^{T_m} \left[ c_{\text{liquid}}(T) - c_{\text{solid}}(T) \right] dT,$$

where $L'(T_i)$ is the effective latent heat released by a droplet initially at the temperature $T_i$, $L_m$ is the latent heat of fusion at the normal melting point, and $c_{\text{liquid}}$ and $c_{\text{solid}}$ are the (temperature dependent) heat capacities of liquid water and ice respectively. $L'$ is plotted as the solid line in the figure. Again, Bertolini et al.'s data fall within the bounds, though (with the exception of three points), their measurements fall below the effective heat released predicted by the equation above.

Why? A thermodynamic state of ice is not fully specified by pressure and temperature. The strain also matters and depends on the history of freezing (See Kostinski and Cantrell (2008) for details.) To summarize here, we again return to the irreversibility of the process. The path we have laid out implicitly assumes that the final state is well characterized by final pressure and temperature. However, rapid freezing is likely to result in ice riddled with defects, thereby affecting it’s entropy.

4. TEMPERATURE GRADIENTS WITHIN THE FREEZING DROPLET AND ASSOCIATED PRODUCTION OF ENTROPY

Release of latent heat must create temperature gradients within the droplet. Indeed, the rate at which liquid is converted to crystal at the ice-water interface is largely controlled by the rate at which the latent heat of fusion is conducted away. Note that this physical picture is consistent with the path used in the derivation of $L'$, where water is warmed to the melting point and then freezes. Surprisingly, entropy production is due to the temperature gradients generated within the droplet.

We estimate the entropy created by the intrinsic irreversibility associated with temperature gradients following the reasoning that the irreversibility can be expressed as the product of the rate of entropy production, $\dot{s}$, and the droplet's thermal relaxation time, $\tau$. (Zemansky, 1981, p. 204). In the expression,

$$\delta s_{irr} = \dot{s} \tau = k d^2 \left( \frac{\Delta T^2}{d^2} \right) \left( \frac{d^2}{\alpha} \right) = \rho c_p d^3 \left( \frac{\Delta T}{T_m} \right)^2,$$

$k$ is the thermal conductivity of water, $d$ is the diameter of the droplet, $\Delta T$ is the temperature gradient, $\alpha$ is the thermal diffusivity of water, $\rho$ is the density of water and $c_p$ is the heat capacity. Normalizing the result by the entropy of the reversible process, $L/T_m$, we obtain:

$$\frac{\delta s_{irr}}{\delta s_{rev}} = c_p \frac{\Delta T}{l T_m^2},$$

where $l$ is the specific latent heat of fusion. The contribution approaches 10% at a supercooling of 40 K. (See Kostinski and Cantrell (2008) for details.)

6. REFERENCES


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