

The heat of freezing for supercooled water: measurements at atmospheric pressure - Supplementary Material

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The temperature dependence of the latent heat of freezing

In the text, we arrive at the equation

$$L_f(T') = L_f(T_m) - \int_{T'}^{T_m} [c_w - c_i] dT \quad (1)$$

using Kirchhoff's relation as a starting point. While Kirchhoff's relation has the advantage of being compact, the physical picture is not as clear. Here we elaborate upon Eq. (1), stressing the physical process. In addition, we show that Eq. (1) follows from using the temperature dependent latent heats of sublimation and vaporization in the triple point identity.

As discussed in Kostinski and Cantrell,¹ the heat released as initially supercooled water freezes can be calculated along a reversible path, assuming the ice is hydrostatic. The reversible path, in pressure and temperature coordinates, consists of warming the supercooled water, freezing at the melting point, then cooling the resulting ice back to the original temperature. This path, in fact, approximates the one taken by droplets as they freeze in the atmosphere. Assuming local thermodynamic equilibrium, the ice-water interface is at the normal melting point. (See discussion in Kostinski and Cantrell. Recent experiments²⁻⁴ lend credence to the basic picture presented there.) Latent heat released at the interface warms water immediately adjacent to it such that all water is warmed from the initially supercooled state to the melting point. The resulting ice then cools back to the ambient temperature. Given the heat capacities of water and ice, the heat exchanged with the reservoir can be calculated through Eq. (1).

That Eq. (1) follows from the triple point identity,

$$L_s = L_f + L_v \quad (2)$$

is not clear. (L_x is the latent heat of sublimation, s , fusion, f , or vaporization, v respectively.) In fact, use of the identity for temperatures other than the triple point must be justified. At the triple point, all three phase changes are reversible, so, using Clausius' formulation of the Second Law of

Thermodynamics, $L_x = T_{triple}\Delta S$ where ΔS is the difference in the entropies of the two phases. For water,

$$T_{triple}(S_i - S_v) = T_{triple}(S_i - S_l) + T_{triple}(S_l - S_v) \quad (3)$$

which reduces to an identity as expected, where S_x is the entropy of ice, vapor or liquid respectively.

In contrast to a transition on the phase boundary, freezing from a metastable state is not reversible, so Eq. (3) cannot be valid as written for any temperature except the triple point. If, however, we assume that the relationship among the latent heats remains the same for temperatures other than the triple point, and employ expressions for the temperature dependent latent heats of sublimation and vaporization along their respective phase boundaries (see below), Eq. (2) becomes

$$L_s(T_m) - \int_{T'}^{T_m} [c_v - c_i]dT = L_f(T') + L_v(T_m) - \int_{T'}^{T_m} [c_v - c_w]dT \quad (4)$$

where c_v is the heat capacity of the vapor, which we have treated as ideal. Note that this step requires reversibility and treats ice as hydrostatic, just as the corresponding steps leading to Eq. (2) in the main body of the text do. The left hand side of Eq. (4) is the temperature dependent latent heat of sublimation while the last two terms on the right hand side correspond to the temperature dependent latent heat of vaporization. A bit of re-arrangement shows that

$$L_f(T') = L_s(T_m) - L_v(T_m) - \int_{T'}^{T_m} [c_w - c_i]dT = L_f(T_m) - \int_{T'}^{T_m} [c_w - c_i]dT. \quad (5)$$

Comparison of Eq. (5) and Eq. (1) shows that using the temperature dependent expressions for the latent heats of sublimation and vaporization in the triple point identity is equivalent to using Kirchhoff's relation for the latent heat of freezing.

Temperature dependence of the latent heat on the phase boundary

The temperature dependence of the latent heat given by integration of Kirchhoff's relation is not valid for paths along the phase boundary since such a path would violate the constant pressure condition imposed in its derivation.

The temperature dependence of the latent heat along the phase boundary can be derived by considering the latent heat as a function of temperature and pressure, then eliminating pressure using the Clausius-Clapeyron equation.^{5,6} The result is

$$\frac{dL}{dT} = \Delta c_p + \frac{L}{T} - L \left(\frac{\partial \ln \Delta v}{\partial T} \right)_p \quad (6)$$

where Δv is the difference in the molar volumes of the two phases on either side of the boundary.

If one of the phases in Equation Eq. (6) is vapor, which is treated as an ideal gas, it reduces to

$$\frac{dL}{dT} = \Delta c_p. \quad (7)$$

Integration of Eq. (7) leads to, using the latent heat of sublimation as an example,

$$L_s(T') = L_s(T_m) + \int_{T'}^{T_m} [c_i - c_v] dT \quad (8)$$

It is this equation which is used above to extend the latent heats of sublimation and vaporization beyond the triple point. Note that it can only be used along the phase boundary, where the condensed phase is in equilibrium with the vapor.

Eq. (7) and Eq. (8) are constrained to the phase boundary, where the phase transition is reversible, because the Second Law is invoked through the use of the Clausius-Clapeyron equation. Recall that the Clausius-Clapeyron Equation, $\frac{dp}{dT} = \frac{L}{T\Delta v}$, is derived from the Clapeyron equation, $\frac{dp}{dT} = \frac{\Delta s}{\Delta v}$ by identifying the change in entropy between the two phases with a definite quantity of

heat at that temperature. That step is valid only when the process is reversible.

References

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