The Temperature Dependence of Water's Latent Heat of Freezing

Anthony Szedlak, Alexandria Johnson[1], Alexander Kostinski, and Will Cantrell

Dept. of Physics and Atmospheric Sciences Program

Michigan Technological University, Houghton MI 49931

Motivating Question

How much heat does a glaciating cloud exchange with the atmosphere as the supercooled droplets of water freeze?

Supercooled liquid water is common in Earth's atmosphere and if/when it freezes, the associated latent heat contributes to cloud buoyancy in the same way that the latent heat of vaporization does. (Of course, the latent heat of vaporization is almost 10 times greater.) To understand the dynamics of ice or mixed phase clouds, the magnitude of that heat exchange must be known.

At the melting point, the phase change releases 6012 J mol^{-1}. Below the melting point, less heat is exchanged.

Kirchhoff's relation

The temperature dependence of the difference in enthalpy between product and reactants for a constant pressure process can be written as:

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

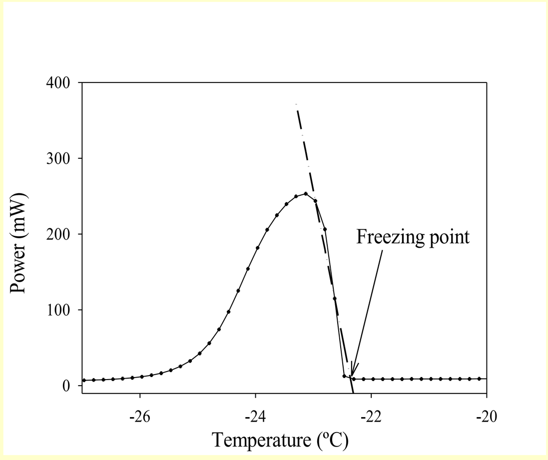
where Δc_p is the difference in the heat capacities. For a melting/freezing transition, $\Delta h = L_f$. The latent heat of fusion for a temperature, T', below the melting point is then:

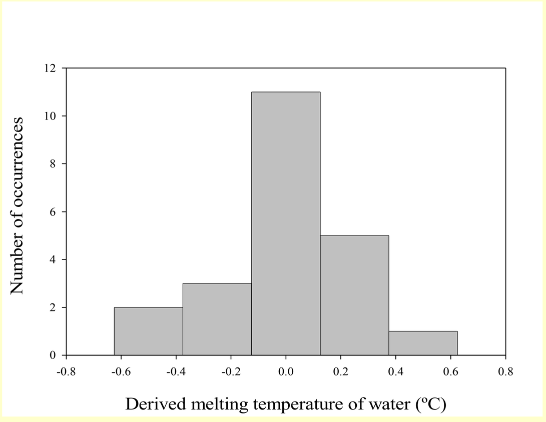
$$L_f(T') = L_f(T_m) - \int_{T'}^{T_m} [c_w - c_i]\, dT$$

where c_w and c_i are the heat capacities of liquid water and ice respectively.

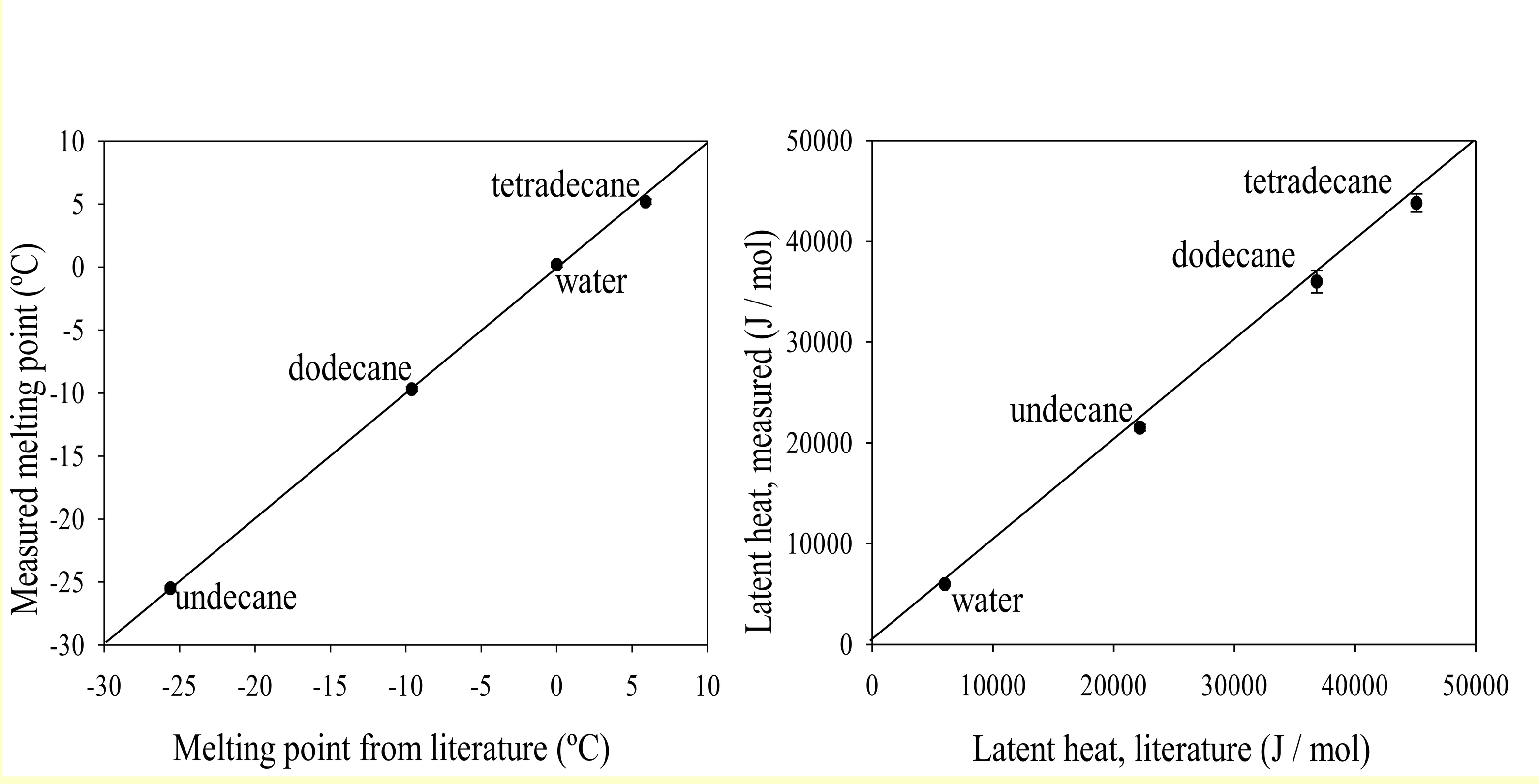
Calorimetry

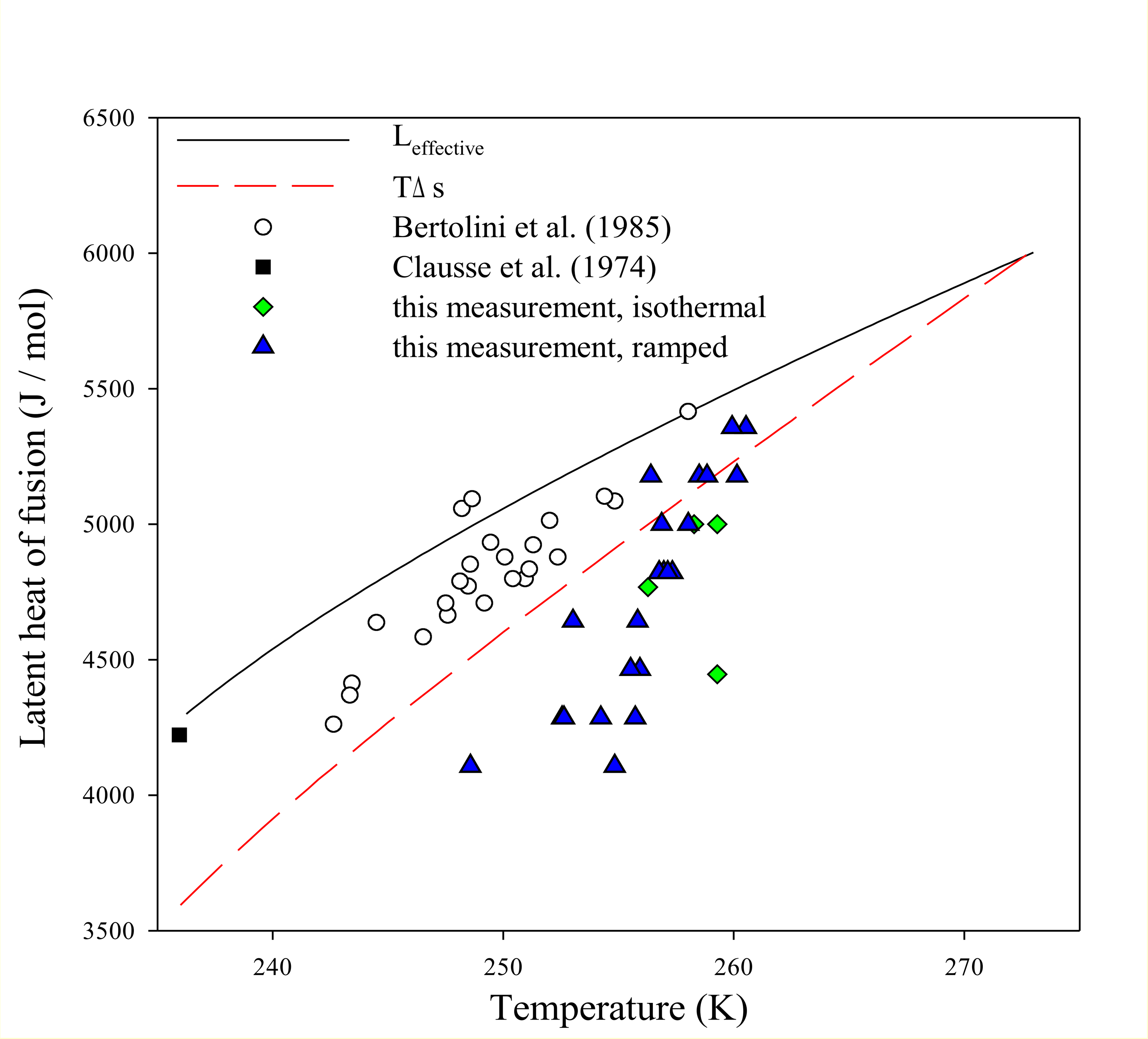
Our measurements are made with a Perkin Elmer DSC 7. A typical freezing curve is shown below. The freezing point is determined from the interception of a line fit to the leading edge of the peak with the baseline. The latent heat is the area under the curve when plotted as power vs. time. The result of a temperature calibration against the melting point of ice Ih is shown in the histogram to the left.





Comparison of the calorimeter's temperature and heat flux calibration against values for dodecane, tetradecane, undecane, and water are shown in the 2 panel figure below. The 1:1 line is shown for reference. Literature values for the alkanes are taken from Finke et al. (1954).





Measured latent heat of freezing

The plot above shows direct, calorimetric measurements of the latent heat of freezing from three different groups, including our own. Also plotted is the integrated form of Kirchhoff's equation ($L_{effective}$ in the figure) and TΔs, where $\Delta s = s_{water} - s_{ice}$. Physically, $L_{effective}$ corresponds to the heat exchange in a reversible process in which supercooled water is warmed to the melting point, freezes, and is then cooled back to the original temperature (see Kostinski and Cantrell, 2008). *TΔs* has limited physical significance. (*TΔs* = 0 is possible if the solid has the same entropy as the supercooled liquid, e.g., at the Kauzmann temperature.)

All of the measurements, except the sole point from Clausse et al., fall below $L_{effective}$. (Bertonlini et al. caution that the two points at ~ 248 K are unreliable; we have included them for the sake of completeness.)

The discrepancy between the measurements and $L_{effective}$ seems paradoxical. *How* can there be a discrepancy? There are no free parameters in Kirchhoff's relation.

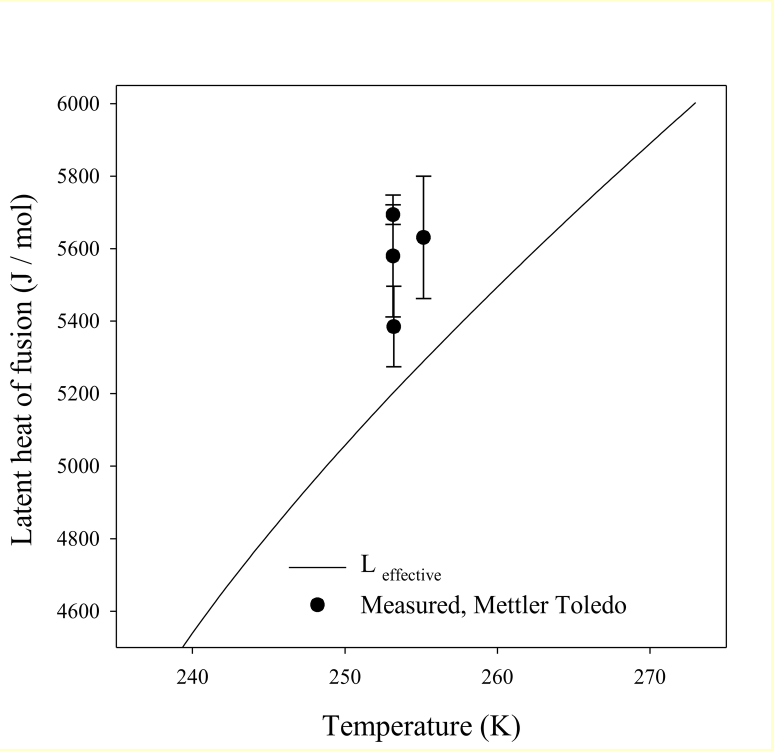
Hurriedly made ice

$L_{effective}$ is calculated from the temperature dependent heat capacities of supercooled, liquid water (Archer and Carter, 2000; Angell et al., 1982) and ice (Haida et al., 1974). Liquid water is hydrostatic, so the initial state of the water is well defined, but the resulting 'ice' need not be ice in equilibrium. In fact, the discrepancy between $L_{effective}$ and their measurements led Bertolini et al. to hypothesize the existence of a metastable, solid form of water.

The latent heat measurements suggest that ice resulting from freezing deeply supercooled water has a higher concentration of defects than does ice in equilibrium at the same temperature and pressure.

Heat exchange depends on how the water freezes (i.e. path)

We believe that the difference between measured values of the latent heat of freezing in the plot to the left is a consequence of different measurement techniques. Our measurements were made with a power compensation DSC. Bertolini's were made with a custom-built instrument. (They measure the temperature increase of the sample cell, produced by the phase transition.)



The figure above shows measurements of the latent heat of freezing, made with a Mettler Toledo Polymer DSC, which is a heat flux calorimeter. The temperature profile in the freezing sample can be very different between instruments because of differences in method of operation. For example, the newly created ice in the Mettler Toledo is at a much higher temperature (near the melting point) than the ice in the Perkin Elmer, which keeps the sample pan at the programmed temperature by decreasing (or increasing) the power to it. (Heat flux DSCs use the temperature difference between the reference and sample pans, which arises from processes within the sample, to calculate the heat flux.) The difference in the sample conditions results in a difference in the heat exchange. In essence, the sample in the Mettler Toledo is self annealing, ironing out the defects introduced in the freezing process whereas the sample in the Perkin Elmer is prevented from reaching temperatures high enough for the defects and imperfections to become mobile, enabling the solid to equilibrate.

Implications for the atmosphere (Returning to the motivating question)

How much heat does a glaciating cloud exchange with the atmosphere?

The deviation of the measurements made with the Perkin Elmer from $L_{effective}$ are a consequence of the efficient heat exchange between water, sample pan, and cooling element. In the atmosphere, the initial stages of freezing are quasi-adiabatic; the transfer of heat from the droplet (water + ice) to the surrounding air is much less efficient than transfer of heat within the drop. Ice in the atmosphere will most likely be self annealed.

Conclusion: $L_{effective}$ is a good approximation to the heat exchange between freezing droplets in a cloud and the surrounding air.

Acknowledgments: Funding from the National Science Foundation (CHE-0410007 and ATM05-54670) is appreciated .

1. Now at Dept. of Earth and Atmospheric Sciences, Purdue University.

References:

Angell, C., M. Oguni, and W. Sichina. *J. Phys. Chem.*, **86**, 998-1002, 1982.
Archer, D. and R. Carter. *J. Phys. Chem.*, **104B**, 8563-8584, 2000.
Bertolini, D., M. Cassettari, and G. Salvetti. *Chem. Phys. Lett.*, **119**, 553-555, 1985.
Clausse, D., J.-P. Dumas, and F. Broto. *C. R. Acad. Sc. Paris, Sèrie B*, **279**, 415–418, 1974.
Haida, O., T. Matsuo, H. Suga, and S. Seki. *J. Chem. Thermodyn.*, **6**, 815-182, 1974.
Finke, H., M. Gross, G. Waddington, and H. Huffman. *J. Am. Chem. Soc.*, **76**, 333–341, 1954.
Kostinski, A. and W. Cantrell. *J. Atmos. Sci.*, **65**, 2961-2971, 2008.