

ALCOHOL CALORIMETRY FOR MEASURING THE

LIQUID WATER FRACTION OF SNOW

David J. Fisk
U.S. Army Cold Regions Research and Engineering Laboratory
Hanover, New Hampshire 03755-1290

ABSTRACT

Equipment and procedure have been devised for measuring the liquid water/ice ratio of snow. The measurement is based on the temperature depression observed on dissolving a 25 g snow sample at 0°C in 80 g methanol at 0°C. The masses of the sample and alcohol are held constant, and the heat of solution of 25 g water in 80 g methanol at 0° is constant, so the only variable is the water/ice ratio in the sample. The solution process occurs quickly enough that it is essentially adiabatic. The latent heat of fusion of up to 8.3 g ice is supplied by the heat of solution of the water in the alcohol. The heat of fusion of any ice above 8.3 g is supplied by a decrease in the solution temperature. Since the total latent heat of fusion varies linearly with ice content, and the solution specific heat is virtually constant, the final solution temperature also varies linearly with sample ice content.

Present equipment has resolution of 0.25% liquid water, by mass, and absolute accuracy of 1%. A single operator can perform four to five measurements per hour.

INTRODUCTION

Most of you have probably heard that liquid water in snow is important. The presence of liquid water means that bonds between snow particles are probably weakening, perhaps increasing avalanche danger. Since the dielectric constants of ice and water are different, water in snow generally affects the performance of electromagnetic remote sensing systems. If your recreation involves sliding on the snow (on skis or dogsleds), water in the snow is likely to affect your speed. If your skis happen to be carrying airplane, wet snow may affect your speed to the extent that your ride home won't get off the ice cap.

Some of you may have been called on to measure snow wetness. So you probably went to the literature and found Yosida's (1966) melting calorimetry method, in which a snow sample is melted in hot water in a Dewar flask, a couple of temperature graphs are extrapolated, and four variables are used to calculate the liquid water fraction, plus or minus several percent. If this wasn't accurate enough for you, you may have frostbitten your hands using freezing calorimetry (Jones 1983), in which a snow sample is frozen by immersion in cold silicone oil, two temperature graphs are extrapolated, and six variables are used to calculate the liquid water fraction to about one percent. Although this is a significant improvement in accuracy, the annoying idiosyncrasies and lymphatic pace of the procedure are strong marks against freezing calorimetry. It requires levels of operator skill and dedication which may not always be available.

I struggled through the winter of 1980-81 using freezing calorimetry in support of microwave testing. Consistent results were elusive, especially with more than one operator. My confidence in the method was abysmal by the season's end. Unfortunately, it was theoretically the most accurate method available.

ETHANOL CALORIMETER

But luck befell me. This laboratory had been examining the use of ethanol (ethyl alcohol) as a drilling fluid for drilling in ice: whenever you drill a hole, some way must be devised to remove the drilled-out material from the hole. We thought that by dumping ethanol in the hole with the drill, the ice chips would simply dissolve away. Well, funds for drilling were cut before we had a chance to try the idea, but not before I had learned a little physical chemistry. What I learned was that when you dissolve ice in ethanol, the mixture cools. When you dissolve water in ethanol, the mixture warms. But if you dissolve a mixture of ice and water in ethanol, the mixture cools, warms, or stays the same, depending on the original ice/water ratio. Furthermore, if the initial masses and temperatures of H₂O (solid and liquid) and ethanol are held constant, and enough ethanol is used to completely dissolve the ice, then the final temperature of the ethanol/water solution is virtually linearly related to the solid/liquid H₂O ratio in the sample. So here was a way to differentiate between ice and water in a snow sample.

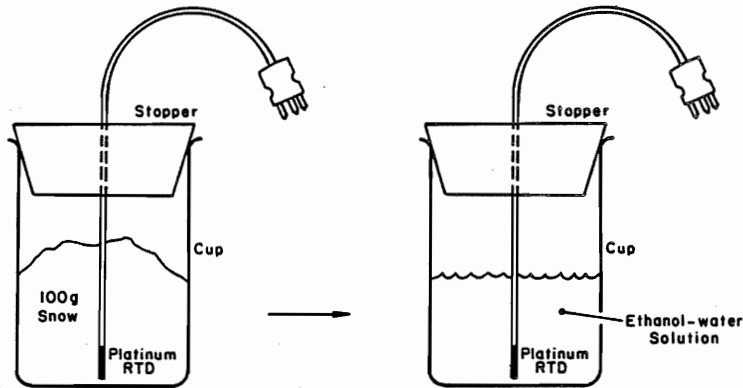


Figure 1. Early alcohol calorimeter consisting of (a) polyethylene cup, (b) polystyrene foam cover, and (c) platinum resistance temperature detector (RTD).

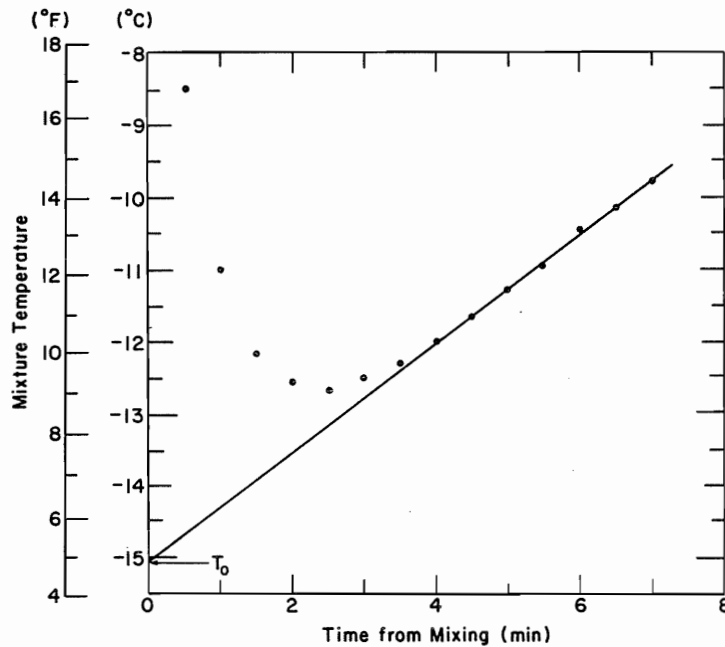


Figure 2. Typical plot of alcohol/sample temperature during an alcohol calorimetry measurement.

I built a simple calorimeter (Fig. 1) and devised a test procedure: The calorimeter is placed in the snow adjacent to the sample site to equilibrate with the snow which, if wet, is at 0°C. Pre-weighed 300 g samples of ethanol are stored in bottles in an ice/water bath to keep them at 0°C. The 0°C calorimeter cup is placed on a balance and 100 g snow is spooned into it. An ethanol bottle is taken from the ice/water bath and dumped into the snow sample, allowing the bottle to drain for about 5 seconds. The cover and temperature sensor are put back on the cup and the assembly is swirled gently for six to seven minutes. The temperature of the mixture is recorded every 30 seconds and plotted to give a curve as shown in Figure 2.

The curved part of the first two to three minutes corresponds to the period when the ice is dissolving. The latter, linear part indicates that all of the ice has dissolved and the solution is warming toward the ambient temperature. The linear part is used to extrapolate to T_0 . This is the temperature which would be observed if the snow were to dissolve instantly and the temperature sensor were to respond instantly. T_0 is related to the mass liquid water fraction of the snow by

$$X_m = \frac{T_0 - T_i}{T_w - T_i}$$

where T_i and T_w are the T_0 values for ice and water at 0°C, determined experimentally. The first calorimeter had $T_i = -16.6^\circ\text{C}$ and $T_w = +8^\circ\text{C}$, so that

$$X_m = \frac{T_0 - (-16.6^\circ)}{8^\circ - (-16.6^\circ)} = \frac{T_0 + 16.6^\circ}{24.6^\circ}$$

T_i and T_w depend on the thermal characteristics of the calorimeter.

I had good results with this calorimeter, but a few refinements were necessary. I wanted to be confident that phase changes weren't occurring in the snow as I weighed it. I was asked if I could reduce the sample size. And since ethanol isn't as easily obtained as other alcohols I decided to try methanol as a working fluid.

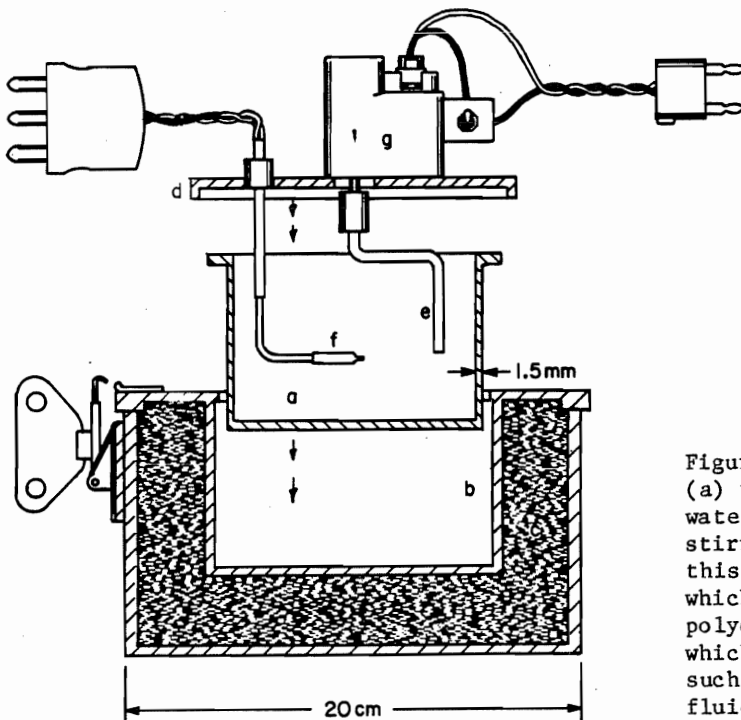


Figure 3. Present alcohol calorimeter: (a) reaction cup, (b) air space, (c) ice-water bath, (d) reaction cup cover, (e) stirrer, (f) platinum RTD. Note that this calorimeter is made of polycarbonate, which is attacked by ethanol. The use of polycarbonate requires that an alcohol which is compatible with polycarbonate, such as methanol, be used as the working fluid.

METHANOL CALORIMETER

The new calorimeter (Fig. 3) has an integral ice/water bath around the reaction cup to help keep the cup at 0°C during snow sample weighing. There is a built-in stirrer, which is motor-operated. The reaction cup is of very low mass to allow the ΔT from 0°C to T_0 to be as great as possible, for better resolution. Sample size was reduced to 25 g, with 80 g methanol to dissolve it. And the whole calorimeter is still light enough to be weighed on a portable electronic balance. The platinum resistance thermometer, built into the cover, has resolution of 0.1°C or F and accuracy of 0.3°.

Snow and methanol are weighed on a balance with resolution of 0.01 g and accuracy of 0.02 g.

When worst-case errors in mass and temperature measurements and in dispensing the methanol accumulate, alcohol calorimetry is accurate to 1% mass liquid water content, or about 0.3% by volume.

I've been using this method in the lab and field since 1981. The small sample requirement allows measurements of very small regions of the snow pack. One operator can make five measurements per hour. The procedure is as accurate as any available, is easy to learn, and more reliable than most.

CONCLUSIONS

Ultimately, snow liquid water content will probably be measured electromagnetically, either remotely or by sensors in the snow. But these methods, for the present, need to be calibrated with a physical method such as calorimetry. So until we all have calibrated devices such as Denoth's probe, there is still a need for calorimetry. And alcohol calorimetry is, I feel, the best of those methods.

REFERENCES

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