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Determination of the Liquid Water Content of Snow by Freezing Calorimetry

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The snow gravimetric liquid water content is perhaps the most important parameter that influences the radar backscatter from a snowpack. This is due to the large difference in the relative dielectric constants of liquid water (≈ 10 - j20 at 35 GHz) and ice (≈ 3.15). Thus even a small amount of liquid water in a snowpack can cause a dramatic change in the backscatter characteristics of the snow.

Freezing calorimetry is widely regarded as the most accurate technique for determining the liquid water content of snow[1 2], although the procedure is tedious and difficult to perform in the field. It is based on straightforward equations of heat transfer. The procedure is relatively simple: a sample of snow of known mass and temperature is added to a calorimeter containing a known mass of a liquid freezing agent. The temperature of the freezing agent is monitored both before and after the snow sample is added. The mixture is agitated until all liquid water in the snow sample has frozen and the mixture has reached an equilibrium temperature. Since the heat capacities of the freezing agent and water and the latent heat of fusion of water are known, the amount of water initially in the liquid state can be determined.

Derivation of Calorimeter Equation

There are two cases, depending on whether the snow "temperature" T_S is above or below T_Z, the freezing point of water (273.15 K or 0 °C). I write "temperature" because the idea of snow temperature is somewhat vague. Snow is a mixture of air, liquid water, and ice. In the following formulation, we assume that the snow is isothermic, that is, it has a constant temperature throughout the sample. If this were true, a snow sample at a temperature above T_Z would be purely liquid, while a sample below T_Z would be completely frozen. Thus our liquid water measurement would be unnecessary, except for the rare case of 0 °C snow. Clearly, snow is not isothermal, even within small samples. We will refer to a snow temperature T_S and understand that this represents a mean temperature which is measured with a thermometer or probe inserted in the snowpack.

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[1]E. B. Jones, *NASA Snowpack Ground-Truth Manual*, NASA CR 170584, May 1983.
[2]W. H. Stiles and F. T. Ulaby, *Microwave Remote Sensing of Snowpacks*, NASA Contractor Report 3263, June 1980.

If the snow temperature T_s is greater than T_z, we have

$$H_f = H_i + \int_{T_s}^{T_z} m_w C_w \, dT + \int_{T_z}^{T_f} m_w C_d \, dT + \int_{T_z}^{T_f} m_d C_d \, dT + \int_{T_i}^{T_f} m_A C_A \, dT + \int_{T_i}^{T_f} m_C C_C \, dT - L m_w \quad [1.a]$$

while for T_s less than T_z, we have

$$H_f = H_i + \int_{T_z}^{T_f} m_w C_d \, dT + \int_{T_s}^{T_f} m_d C_d \, dT + \int_{T_i}^{T_f} m_A C_A \, dT + \int_{T_i}^{T_f} m_C C_C \, dT - L m_w \quad [1.b]$$

where

H_f = final heat of calorimeter system (cal)

H_i = initial heat of calorimeter system (cal) = H_f

m_w = mass of liquid water in the snow (g)

m_d = mass of solid component of snow (g)

m_s = mass of snow (including both liquid and solid components) (g)

m_A = mass of freezing agent (g)

m_C = mass of calorimeter (g)

L = latent heat of fusion of water (cal/g) = 79.7 cal/g

C_w = heat capacity of liquid water ($cal \cdot g^{-1} \cdot K^{-1}$)

C_d = heat capacity of frozen water ($cal \cdot g^{-1} \cdot K^{-1}$)

C_A = heat capacity of freezing agent ($cal \cdot g^{-1} \cdot K^{-1}$)

C_C = heat capacity of calorimeter ($cal \cdot g^{-1} \cdot K^{-1}$)

T_i = initial temperature of freezing agent (K)

T_f = final temperature of freezing agent/snow mixture (K)

T_z = freezing point of water (K) = 273.15 K

T_s = temperature of snow sample (K)

In addition to the initial and final heats of the system, there are six terms in equations [1.a] and [1.b]:

(1) the heat lost by liquid water in the snow as it cools to 273.15 K,

(2) the heat lost by liquid water at 273.15 K as it freezes,

(3) the heat lost by the liquid water (after freezing) as it cools from 273.15 K to the final temperature,

(4) the heat lost by the frozen water in the snow (i.e., the ice crystals in the sample) as it cools from its initial temperature to its final temperature,

(5) the heat gained by the calorimeter as it warms to the final temperature, and

(6) the heat gained by the freezing agent as it warms to the final temperature.

Note that term (1) vanishes if $T_S < T_Z$ (Eq. [1.b]). In the above equations, we have assumed that the liquid and solid components of the snow mixture fit one of the following descriptions:

a. the liquid component has temperature T_S ($> T_Z$) and the solid component is at T_Z;

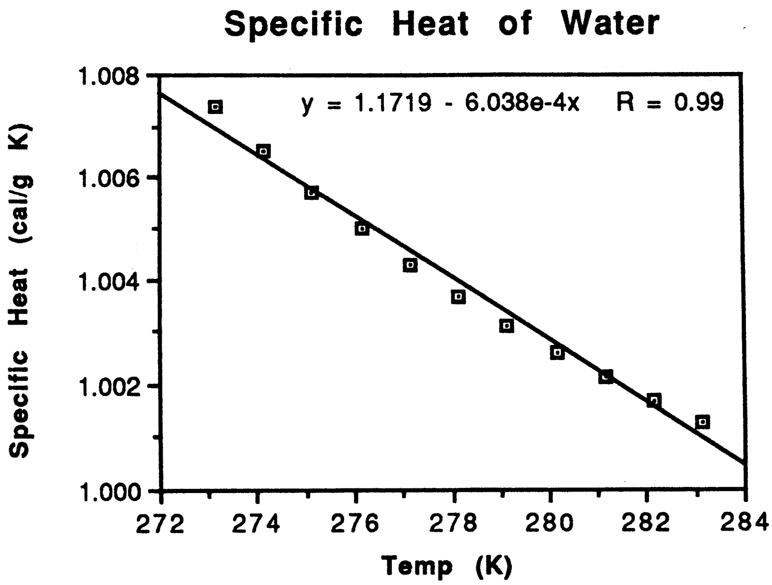
b. the liquid and solid components are at $T_S = T_Z$; or

c. the liquid component is at T_Z and the solid component is at T_S ($< T_Z$).

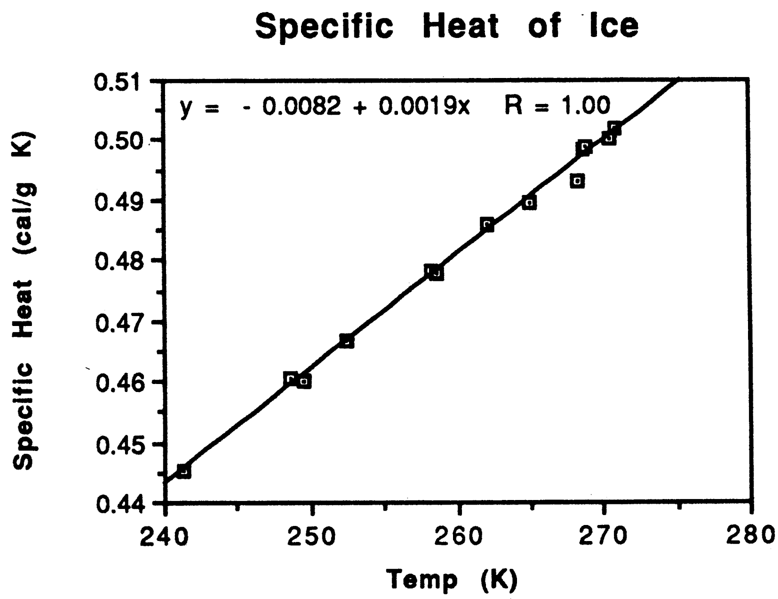
In other words, we cannot have $T_{liquid} > 273.15$ K and $T_{solid} < 273.15$ K simultaneously.

We now solve for each case separately, using some simplifying assumptions. First, we assume that the heat capacities (specific heat) of liquid water, ice, and the freezing agent are linear functions of temperature. These are not bad assumptions over the temperature ranges in which we work. The values for the heat capacity of liquid water[3] are shown in the following graph:

[3]Values obtained from CRC *Handbook of Chemistry and Physics*, 60th Edition, p. D-74.



Values of the heat capacity of ice are shown below[4]:



The determination of the heat capacity of the freezing agent will be described in a later section. A further simplification is performed by assigning a "calorimeter constant", *E*, with units of grams of the freezing agent. This allows the calorimeter and freezing agent to be lumped into a single term. Using the above two assumptions results in the following equations:

[4]Values obtained from *CRC Handbook of Chemistry and Physics*, 60th Edition, p. D-175.

for $T_s \geq T_z$

$$0 = m_w C_{wsz}(T_z - T_s) + m_w C_{dzf}(T_f - T_z) + (m_s - m_w)C_{dzf}(T_f - T_z) + (m_A + E)C_{Aif}(T_f - T_i) - Lm_w \quad [2.a]$$

for $T_s \leq T_z$

$$0 = m_w C_{dzf}(T_f - T_z) + (m_s - m_w)C_{dsf}(T_f - T_s) + (m_A + E)C_{Aif}(T_f - T_i) - Lm_w \quad [2.b]$$

where we have evaluated the integrals using the midpoint rule for linear functions. Terms of the form C_{abc} represent the heat capacity of a at the average of temperatures T_b and T_c ; for example, C_{wsz} represents the heat capacity of liquid water at temperature $(T_s + T_z)/2$. These equations can now be solved for the fraction of liquid water mass:

$$\frac{m_w}{m_s} = \frac{(m_A + E)C_{Aif}(T_f - T_i) - m_s C_{dzf}(T_z - T_f)}{m_s[L + C_{wsz}(T_s - T_z)]}, \quad (T_s \geq T_z) \quad [3.a]$$

$$\frac{m_w}{m_s} = \frac{(m_A + E)C_{Aif}(T_f - T_i) - m_s C_{dsf}(T_s - T_f)}{m_s[L - C_{dsf}(T_s - T_f) + C_{dzf}(T_z - T_f)]}, \quad (T_s \leq T_z) \quad [3.b]$$

These equations vary slightly from the equation used in the *NASA Snowpack Ground Truth Manual,* in which the additional assumptions are made that T_s is always less than or equal to the freezing point of water and term (3) described above is approximated by the heat lost by the liquid water after freezing as it cools from the snow temperature T_s (rather than from 273.15 K) to the final temperature.

Calorimeter Constant

The calorimeter constant E must be determined before liquid water content measurements can be made. The procedure for determining the calorimeter constant is similar to the liquid water content measurement; the difference is that the freezing agent and quantity of liquid water are known exactly, resulting in a single unknown in the calorimeter equation, which is the calorimeter constant.

The freezing agent used in the 1989 snow experiments was a silicon oil. Since the heat capacity of the oil had not yet been determined, ethanol was used as a freezing agent in the determination of the calorimeter constant. Ethanol (200 proof) was obtained from University Stores.

The heat capacity of ethanol is well-known and was obtained from Brown and Ziegler (1979)[5], which gives a fourth-degree polynomial for the heat

[5]G. Nelson Brown, Jr., and Waldemer T. Ziegler, "Temperature Dependence of Excess Thermodynamic Properties of Ethanol + n-Heptane and 2-Propanol + n-Heptane Solutions", *Journal of Chemical and Engineering Data,* Vol. 24, Number 4, 1979, pp. 319-330.

capacity in the temperature range $159\text{ K} \le T \le 306\text{ K}$. The equation used for determining the calorimeter constant can be derived from

$$H_f = H_i + \int_{T_i}^{T_f} m_{ce} C_e(T)\, dT + \int_{T_w}^{T_f} m_{we} C_e(T)\, dT + \int_{T_i}^{T_f} m_C C_C(T)\, dT \qquad [4]$$

where

H_f = final heat of calorimeter system (cal)

H_i = initial heat of calorimeter system (cal) = H_f

m_{ce} = mass of cold ethanol (g)

m_{we} = mass of warm ethanol (g)

m_C = mass of calorimeter (g)

$C_e(T)$ = heat capacity of ethanol ($\text{cal} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$)

$C_C(T)$ = heat capacity of calorimeter ($\text{cal} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$)

T_i = initial temperature of cold ethanol (K)

T_f = final temperature of ethanol (K)

T_w = initial temperature of warm ethanol (K)

The product $m_C C_C(T)$ is replaced by $E_e C_e(T)$, where E_e is the calorimeter constant in grams of ethanol. Solving for E_e:

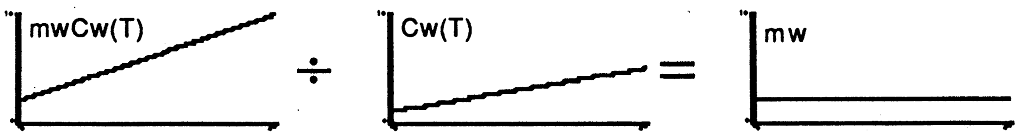
$$E_e = \left[m_{we} \int_{T_f}^{T_w} C_e(T)\, dT \right] \left[\int_{T_i}^{T_f} C_e(T)\, dT \right]^{-1} - m_{ce} \qquad [5]$$

Although $C_e(T)$ is almost linear in the region of integration, the integrations were performed analytically on the fourth-order polynomials. The procedure for obtaining the actual masses and temperatures to use in the above equation is exactly like that used in the snow measurements, except that warm and cold ethanol are used in place of a snow sample and freezing agent. The procedure and data reduction are described fully in the section on snow measurements.

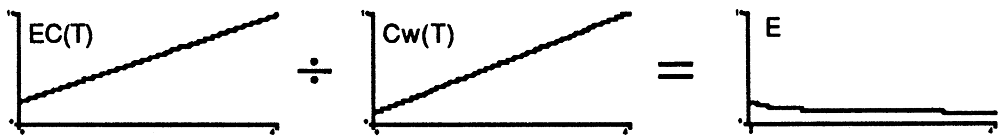
The calorimeter used was an Aladdin Stanley insulated bottle with a hole drilled in the lid for the temperature probe. After it became apparent that inversion of the calorimeter was necessary to obtain good mixing of the freezing agent and a uniform inner temperature, silicon sealant was used to seal around the thermal probe. Also, the original circular rubber seal under the lid had to be replaced because it became too stiff when exposed to the cold (≈ -50 °C) ethanol and tended to leak. A new seal was cut from a sheet of neoprene rubber; it sealed much better.

There is a question as to whether the concept of a "calorimeter constant" is valid at all. In all the calorimetric formulations studied (including the one above), the assumption has been made that $m_C C_C(T) = E_A C_A(T)$, where E_A is the calorimeter constant in grams of the freezing agent (oil, ethanol, etc.). This is not true in general over a temperature range—it implies that the thermal response of the calorimeter is just like E_A grams of the freezing agent. Such an approximation may be permissible over a small range of temperature, but is probably not true over large temperature ranges.

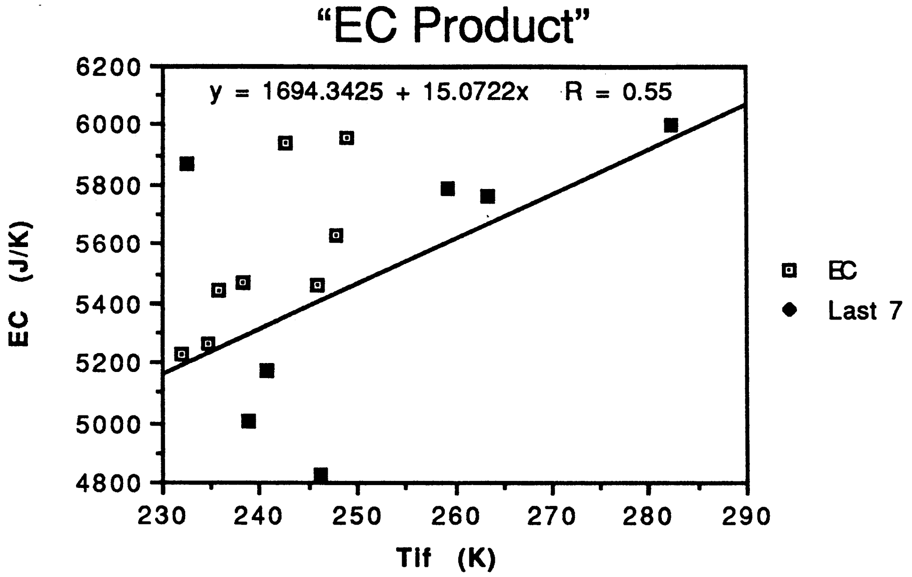
Consider: when we are solving for the amount of liquid water, we obtain the product $m_w C_w$, where C_w is at temperature $(T_i + T_f) / 2$, and we know that $C_w(T)$ is linear with T. Since C_w(T) is known, we can solve for the corresponding m_w, and we should get the same value regardless of temperature.



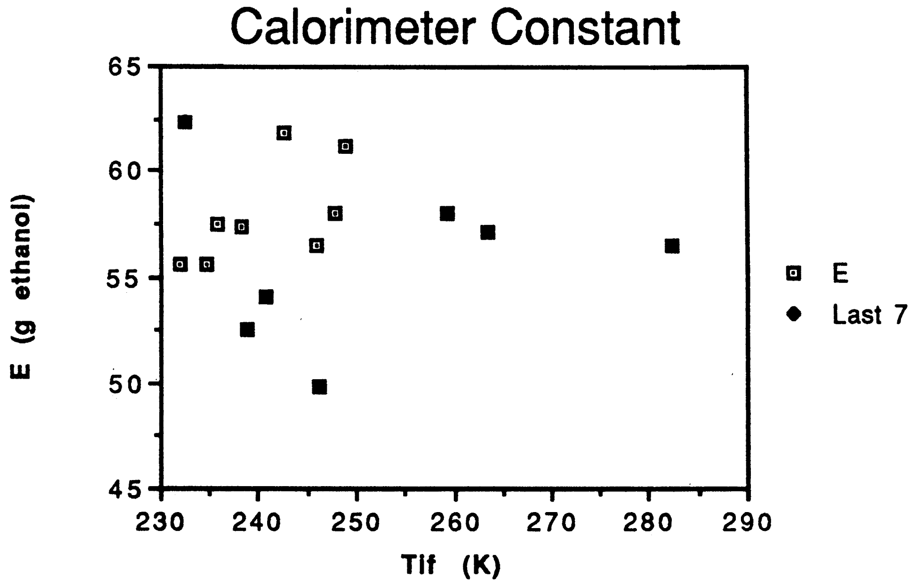
Similarly, we measure the "*EC*" curve of the calorimeter, where its mass is represented by *E*, the calorimeter constant. We're probably safe in assuming that *EC* is linear with *T*, but we have no guarantee that the *EC* curve is a constant multiple of the heat capacity curve of the oil or ethanol. For example, if the *EC* curve is not as steep, we obtain a temperature-dependent value of *E*:



In spite of the above arguments, we have had to use the idea of a calorimeter constant. This was due to my inability to measure the "*EC* product" as a function of temperature. The fifteen "good" calorimeter calibrations are shown in the figure below—the last seven are solid black. These seven were, in my opinion, the most carefully executed; however, they did not result in a nice linear curve for *EC*(*T*):



Part of the scatter here could probably have been reduced through a much larger number of trials, but there was not sufficient time to complete such trials. The known heat capacity of ethanol $C_e(T)$ was divided out of the above data, resulting in the following plot:



The last seven points (in black) were averaged to obtain a value of 56.91 g ethanol for the calorimeter constant. The standard deviation of these points was 3.34 g (standard deviation/mean = 0.06). We therefore used this value and hoped that the resulting error was not large compared to other errors in our measurements. According to Tom Haddock, the heat capacity of the calorimeter should not change significantly with temperature.

Heat Capacity of Silicon Oil

The next task was to determine, as a function of temperature, the heat capacity of the silicon oil which served as the freezing agent in the liquid water content measurements. Silicon oil was recommended by Bruce Jones, author of the *NASA Snowpack Ground Truth Manual,* for its reusability and safety. Toluene had been used previously as a freezing agent, but its low flash point and toxic fumes made its use undesirable. The oil used was Dow Corning 200 fluid (a dimethylpolysiloxane), 5 centistokes viscosity.

The heat capacity of the oil was assumed to be linear, in accordance with Jones (1983). The equation used was that given originally for snow measurements [1.a] with T_s replaced by T_w, modified for the case where the water sample is completely liquid:

$$H_f = H_i + \int_{T_w}^{T_z} m_w C_w \, dT + \int_{T_z}^{T_f} m_w C_d \, dT + \int_{T_i}^{T_f} m_o C_o \, dT + \int_{T_i}^{T_f} m_C C_C \, dT - L m_w \qquad [6]$$

Having assumed that all heat capacities are linear functions of temperature, we can write

$$0 = m_w C_{wwz}(T_z - T_w) + m_w C_{dzf}(T_f - T_z) + m_o C_{ofi}(T_f - T_i) + m_C C_{Cfi}(T_f - T_i) - L m_w \qquad [7]$$

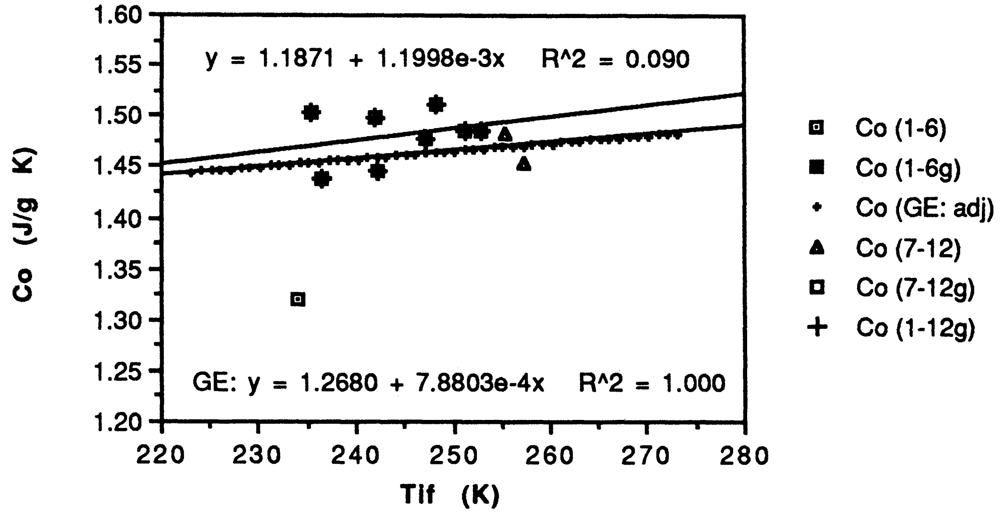
Converting to a calorimeter constant E_o:

$$m_C C_{Cfi} = E_o C_{ofi} \qquad [8]$$

At a given temperature, $E_e C_e = E_o C_o$. We can therefore solve for C_{ofi}:

$$C_{ofi} = \frac{m_w[C_{wwz}(T_w - T_z) + C_{dzf}(T_z - T_f) + L] - E_e C_{efi}(T_f - T_i)}{m_o(T_f - T_i)} \qquad [9]$$

After several trials, a curve of C_0 values was obtained, as shown below.



The legend notations are explained as follows: Co (1-6), oil heat capacity measurements 1-6; Co (1-6g), the "good" measurements from measurements 1-6; Co (GE: adj), values given in Jones (1983) for silicon fluid minus a constant (this was plotted to see if our fluid's heat capacity had the same slope); Co (7-12), oil heat capacity measurements 7-12; Co (7-12g), the "good" measurements from measurements 7-12; Co (1-12g), "good" measurements from the entire set of twelve. A line was fit to the values in the last group, Co (1-12g); its equation is shown at the top of the graph.

Next a value was obtained for E_0, the calorimeter constant in grams of oil. We chose 233.6 K (by averaging the first nine values of T_{if} in the oil measurements) as the temperature at which we would solve $E_eC_e = E_0C_0$ for E_0. The resulting value of E_0 was 80.34 g oil.

Necessary Equipment

The following is a description of the equipment used in the field for liquid water measurements at the Brighton experiment site during the winter of 1989:

1. **Calorimeter** The calorimeter consisted of an Aladdin Stanley Thermos-type wide-mouth insulating bottle (24 ounce size). A small hole was drilled in the lid to allow the insertion of a metallic probe tip containing a 4-wire RTD sensor. The probe fit very snugly into the hole; its diameter was about 8 mm. Silicone sealant was used to seal the lid around the probe. Caution is advised when handling the lid/probe assembly to avoid turning

the probe in its hole and breaking the seal. The probe extended about 13 cm into the interior of the calorimeter.

2. **HP3468A Digital Multimeter with HPIL option** The multimeter was used to monitor the resistance of the RTD probe. The HP-41CX calculator obtained resistance values every 15 seconds and converted the resistance to a temperature. The 4-wire resistance mode was used to increase accuracy.

3. **HP-41CX (or compatible) calculator** The programmable calculator recorded the calorimeter temperature at 15-second intervals by obtaining the RTD resistance from the multimeter and converting the resistance to a temperature value. Resistance, time, and temperature values were recorded on an HP Thermal Printer for later data reduction. Use of the programmable calculator made the temperature monitoring process almost automatic. (The program used for these measurements is listed at the end of this report.)

4. **Connecting cord from RTD to multimeter.**

5. **HP-IL Module and IL patch cord.**

6. **HP82143A Thermal Printer and thermal printer paper (black).**

7. **Outlet Strip and Extension Cord** (long enough to reach nearest AC outlet)

8. **Electronic Scale** The electronic scale is a necessity if measurements are to be made at a reasonable rate. Our electronic scale was enclosed in a plastic carrying box with internal heater to isolate the scale from the wind and keep it warm enough to function (the scale was not designed to operate near 0 °C).

9. **Supply of silicon oil** We put silicon oil in 300 ml polyprophylene bottles for ease of use. Each bottle contained enough freezing agent for one measurement run. The bottles were not breakable, were easy to handle, and could be cooled to -40 to -50 °C.

10. **Dry Ice and Cooler** The bottles of freezing agent are placed in the cooler with dry ice until cooled to a temperature of approximately -40 to -50 °C. The dry ice will last about two days in the cooler when purchased in a 50 pound cake.

11. **Plastic containers for "wet" oil** The oil/ice mixture is dumped into this container after each measurement. Although the large chunks of ice can be strained out by the funnel, the smaller bits of ice must be removed later. The majority of the oil can be recovered. Plastic jugs, such as those used for milk or distilled water, work well.

12. **Funnels** Separate plastic funnels are needed for pouring into the calorimeter and the wet oil container. Large funnels are easier to use when wearing gloves.

13. **Paper towels and dish washing tool** The calorimeter must be thoroughly cleaned after each measurement. A large supply of paper towels and a dish-washing tool (the type with a sponge attached to a hollow plastic handle) work well for drying or wiping out the inside of the calorimeter.

14. **Garbage bags** For all those used paper towels.

15. **Mercury thermometers** for measuring the temperature of the snow sample. These are very fragile, so several extras should be available. The mercury thermometers seemed more reliable than the electronic thermometer.

16. **Plastic scoop** Used to collect the snow sample.

17. **HP Data Cassette Drive (optional)** The measurement program is stored on a program cassette. If the calculator loses the program for some reason, having the cassette and cassette drive in the field or nearby will save an unnecessary trip back to the lab. The drive and cassette should probably be kept in a warm place when not being used.

Preparation

The calorimetric measurements should be conducted in a location which is sheltered from the wind but still at ambient temperature. A table of some sort is needed for the various equipment, and AC power needs to be available within a reasonable distance (closer than the end of your extension cord). It is best to cover the table area with paper towels or plastic before setting up the equipment; this will protect the surface from the oil which will be spilled on it. Plug in the electronic scale first to allow it to warm up. Next, set up the digital multimeter, printer, and calculator. The HP-41CX calculator, thermal printer, and digital multimeter must be connected via the HP interface loop so that the calculator can control the multimeter and process and record the results. A schematic of the set-up is shown below. The procedure for connecting the devices is as follows:

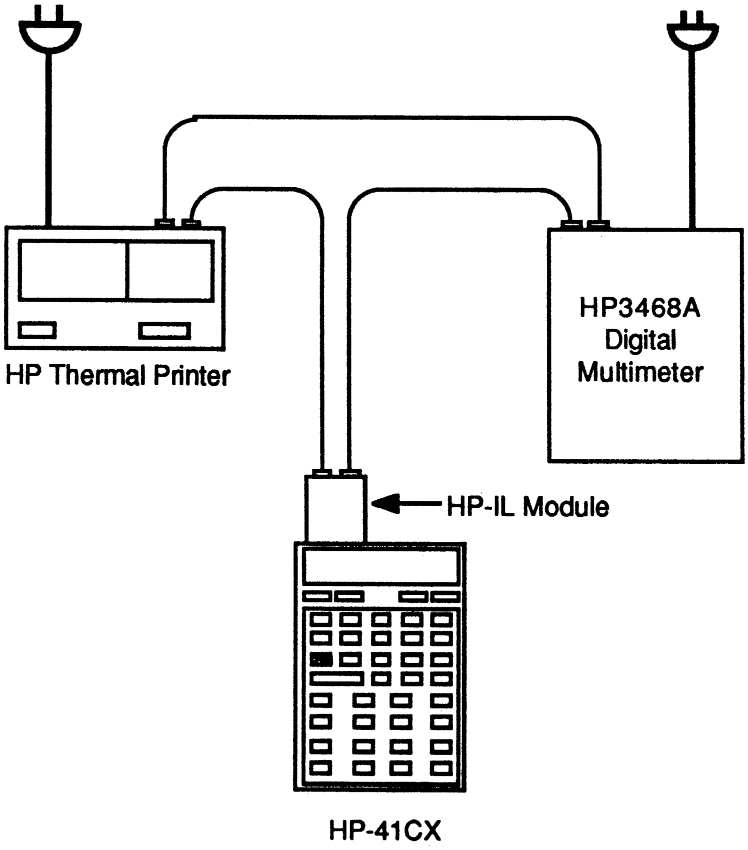
a. **MAKE SURE THE HP-41CX CALCULATOR IS OFF.** This is very important! Connecting or disconnecting the HP-IL module while the calculator is on can result in loss of program memory, which means that you will have to reload the program from tape.

b. Insert the HP-IL module into any of the ports on the rear of the HP-41CX. (Keep the port cover handy—you will want to replace it when you are finished.)

c. Connect the cables extending from the HP-IL module to the multimeter and the printer—it does not matter which cable goes to which device.

d. Use a jumper cable to connect the multimeter and printer directly to each other, thus completing the loop.

e. Plug in the AC power cords of the printer, multimeter, and calculator.



f. Connect the RTD probe cables to the front of the multimeter (4-wire Ω terminals).

g. Turn on the printer and multimeter.

h. Turn on the HP-41CX.

i. Press [XEQ], [ALPHA], [O], [N], [ALPHA]. ([key] indicates a key with the label *key;* in Alpha mode, the single letters are marked in blue on the keys). This will prevent the calculator from shutting itself off after 10 minutes of inactivity.

i. Press [XEQ], [ALPHA], [T], [E], [M], [P], [ALPHA] to start the calorimeter program.

j. The multimeter will change to 4-wire Ω. The "REMOTE" indicator will appear on the multimeter display, indicating that it is being controlled remotely. To make any changes to multimeter settings manually, the LOCAL button must first be pressed. The printer will print a horizontal line.

k. The prompt "EMPTY MASS?" will appear on the calculator.

The calorimeter should be cooled before the first measurement. Cool the calorimeter by pouring in one bottle of freezing agent and waiting several minutes. The freezing agent can then be poured back into its bottle, re-cooled, and used later. The freezing agent should have a temperature of -40 to -50 °C (it must be cold enough so that the final temperature after adding the snow sample is still below 0 °C). Be sure to wipe the inside of the calorimeter before the first measurement. Put the thermometers and snow scoop by the snow pit or sample site.

Measurement Procedure

When ready to begin a measurement, the calculator should be displaying the "EMPTY MASS?" prompt. If not, press [XEQ], [ALPHA], [T], [E], [M], [P], and [ALPHA] to start the calorimeter program. The measurement sequence has the following steps:

a. Place the empty calorimeter (without the lid) on the electronic scale. Enter the displayed mass (in grams) into the calculator and press [R/S]. The "MASS W/OIL?" prompt will appear.

b. Pour one bottle of freezing agent into the calorimeter. Place the calorimeter (without the lid) on the electronic scale, and enter the mass (in grams) into the calculator and press [R/S]. The "R/S TO BEGIN" prompt will appear.

c. Put the lid on the calorimeter and tighten it securely. Be careful not to twist the probe in the lid. Press [R/S]. The "‹A› TO ADD" prompt will appear.

d. Agitate the calorimeter by inverting it continuously. A complete up-down-up sequence should take approximately two seconds. Be careful not to pull on the RTD wires.

Every 15 seconds, the calculator will beep, indicating that the temperature in the calorimeter has been measured via the multimeter and RTD sensor. After the beep, the printer will print the elapsed time in minutes and seconds, the elapsed time in seconds, the freezing agent temperature in degrees Celsius, the freezing agent temperature in kelvins, and the change in temperature from the previous reading. Since the calorimeter is not perfectly insulated, heat will leak in through the walls and lid. The agitation should be continued until the rate of temperature change is roughly constant, indicating that the interior of the calorimeter is at a uniform temperature which is rising steadily due to heat leakage. This usually happens within 5 to 7 minutes. The "equilibrium" temperature rise rate is usually between 0.01 K and 0.1 K in 15 seconds, depending on the absolute temperature.

e. When the temperature is rising at a constant (or nearly constant) rate for 90-120 seconds, you are ready to add the snow sample. Press [A]. The calculator will sound a sequence of four tones, and the "SNOW TEMP? C" prompt will appear.

f. Collect the snow sample in the plastic scoop, noting the snow temperature (or ideally, have an assistant do it). Enter the snow temperature in degrees Celsius and press [R/S]. The "R/S WHEN ADD." prompt will appear.

g. Open the calorimeter and dump the snow sample in. Press [R/S] at the moment the snow sample is added to the freezing agent. The printer will print a record of the elapsed time when the snow sample was added in minutes and seconds and in seconds only.

h. Close the calorimeter and shake the calorimeter vigorously to mix the freezing agent and snow sample thoroughly. Continue agitating the calorimeter as before. The temperature readings will begin 60-90 seconds after the snow sample was added, and the "‹A› TO STOP" prompt will appear.

i. When the temperature is again rising at a constant (or nearly constant) rate for 90-120 seconds, press [A] to stop the automatic temperature recording. Stop agitating the calorimeter. The calculator will sound a sequence of four tones, and the "TOTAL MASS?" prompt will appear.

j. Remove the lid of the calorimeter, making sure that no large pieces of ice cling to the temperature probe. Place the calorimeter (without the lid) on the electronic scale, and enter the mass (in grams) into the calculator and press [R/S]. The printer will print the mass of the snow sample, the mass of the freezing agent, and the temperature of the snow sample prior to being added to the calorimeter. The printer will then advance the paper several lines, and the program will stop. (Press [XEQ], [ALPHA], [T], [E], [M], [P], [ALPHA] when ready to start the next measurement.)

k. Pour the freezing agent/ice mixture through a filtering funnel into the wet oil container. Any ice remaining in the funnel may be discarded into a garbage bag.

l. Wipe the calorimeter lid and temperature probe dry with paper towels. Wipe the inside of the calorimeter dry using paper towels and the dish-washing tool. Several paper towels will be needed. Discard the used towels in the garbage bag.

The average time for a complete measurement sequence, including cleanup, is 35-40 minutes. The fastest I have been able to complete the sequence is about 30 minutes, though I think this could be reduced slightly with an assistant. It is extremely difficult to maintain a 30-minute sampling rate without an assistant.

Oil Recovery

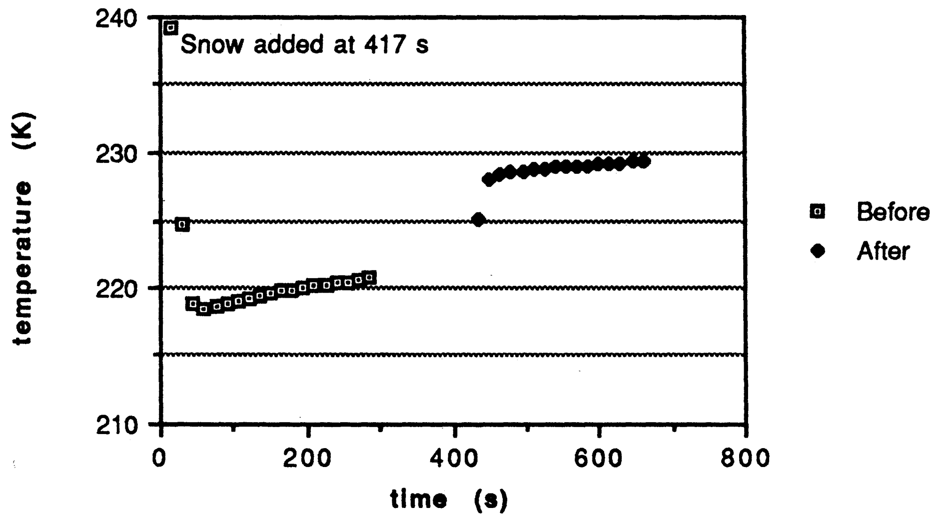
Most of the oil used as freezing agent can be recovered for re-use. A large portion of the ice in the oil can be removed by (1) allowing the wet oil container to warm up enough so that the ice particles melt and move to the bottom of the oil, (2) re-cooling the container so that the water layer re-freezes, and (3) pouring the oil into another container (the ice layer will be trapped in the original container, since it is too large to pass through the spout of the container).

A second step, performed in the laboratory, removes small quantities of water and other particles by use of a separating funnel and careful pouring. The separating funnel is a glass funnel with a stopcock valve at the bottom. After allowing the wet oil to warm to room temperature and the water and other solids to collect at the bottom of the container, carefully pour some oil (which is on top) into the separating funnel. After inspecting the oil in the funnel visually, some or all can be added to the "dry oil" container or discarded, if water or other impurities are present. Do not try to pour all the oil layer out of the wet oil container—you will invariably get some of the water layer, too. Some of the oil will be lost, but it is better to lose some oil each time than to contaminate the freezing agent.

Data Reduction

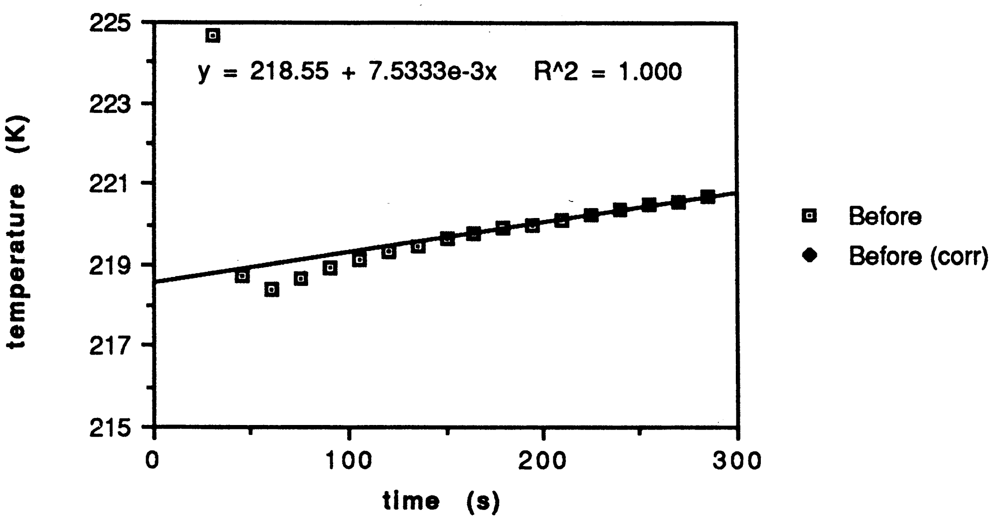
In order to use the formulas described earlier in this report, it is necessary to extrapolate the measured temperatures forward or backward to the time that the snow sample is added to the calorimeter. The assumption is that the heat transfer can be treated as if it occurred instantaneously; therefore, we need to determine the "initial" and "final" temperatures of the contents of the calorimeter, where "initial" and "final" refer to the instants just before and just after the snow sample is added.

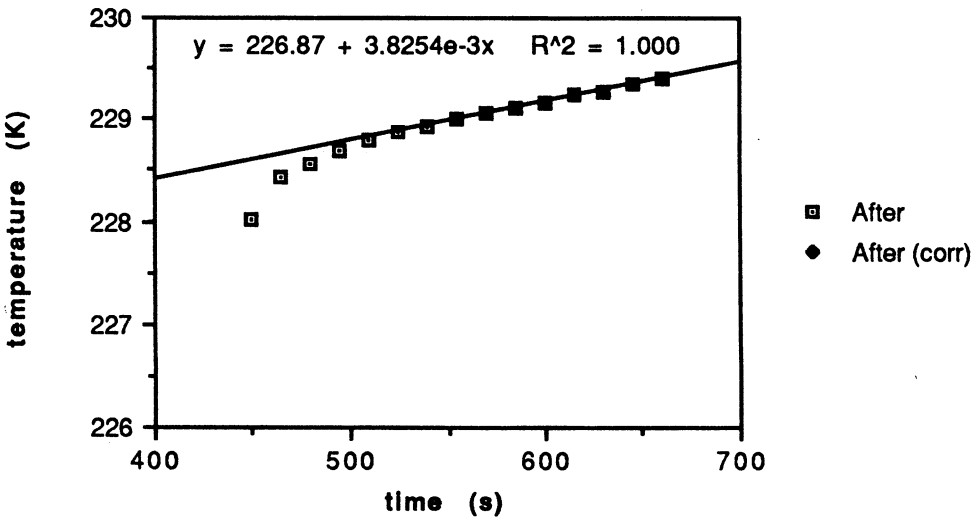
The temperature readings for a given measurement sequence are entered into a Cricket Graph[6] data file along with the corresponding measurement times to produce a graph of temperature vs. time, as shown below:



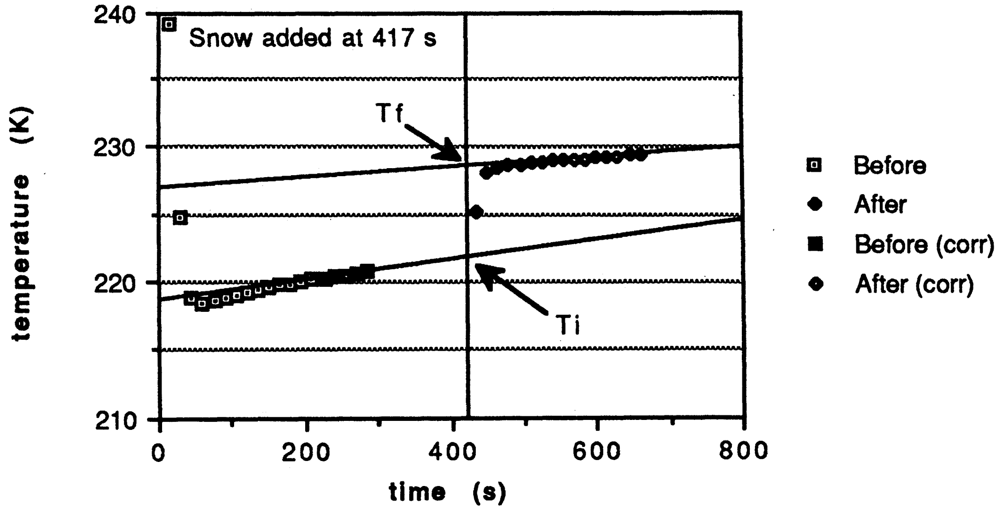
When the freezing agent or the snow sample is added to the calorimeter, the measured temperature changes suddenly and then approaches a linear increase. It is this linear temperature curve which we wish to extrapolate. To do this, the data points which indicate a linear trend (after the initial fluctuation) are copied into another column in the Cricket Graph data file and plotted. The Simple curve fit option is used to fit a line to these points. The coefficients associated with this line will be used in the next step in the data reduction. Typical plots are shown here (from file 8903020738):

[6]Copyright © 1986/87/88 Cricket Software.





Note that each measurement will have two line fits associated with it: a "before" and an "after" line. The three graphs (original, before, and after) are printed and retained for reference later. The extrapolated lines and resultant "initial" and "final" temperatures are shown below:



After performing the graphical portion of the data reduction, the masses, temperatures, and linear coefficients were entered into an Excel[7] spreadsheet which was constructed using the formulas described previously. (A copy of the spreadsheet is included at the end of this report.) The spreadsheet calculates all intermediate results and the gravimetric snow liquid water content. By entering the snow density, the spreadsheet can also print the volumetric snow liquid water content.

[7]Microsoft ® Excel, © 1985-1988 Microsoft Corp.

Excel spreadsheet for reduction of liquid water data

	1	2
8	**Date:**	31087
9	**Time (EST):**	0.691666666666667
10		
11	**Data Set (YYMMDDhhmm):**	8902101636
12		
13	**Before Adding Snow:**	
14	Intercept	230.1485
15	Slope	0.0072
16		
17	**After Adding Snow:**	
18	Intercept	235.9242
19	Slope	0.0045
20		
21	**Snow added at (s):**	439
22		
23	**Masses (g):**	
24	Freezing Agent (Oil)	356.5
25	Snow	47.2
26		
27	**Snow Temperature Ts (K)**	269
28		
29	**Ti (K)**	=mb*x+bb
30		
31	**Tf (K)**	=ma*x+ba
32		
33	**Tif (K)**	=(Ti+Tf)/2
34		
35	**Tzf (K)**	=(Tz+Tf)/2
36		
37	**Tsz (K)**	=(Ts+Tz)/2
38		
39	**Tsf (K)**	=(Ts+Tf)/2
40		
41	**Ts (°C)**	=Ts-273.15
42		
43	**Ts > Tz? (1 = yes, 0 = no)**	=SIGN(SIGN(TsC)+ABS(SIGN(TsC)))
44		
45	**Ts ≤ Tz? (1 = yes, 0 = no)**	=ABS(SIGN(SIGN(TsC)-1))
46		
47	**Colf (J/g K)**	=ao*Tif+bo
48		
49	**Clzf (cal/g K)**	=ai*Tzf+bi
50	**Clzf (J/g K)**	=R[-1]C/calj

	1	2
51		
52	**Cwsz (cal/g K)**	=aw*Tsz+bw
53	**Cwsz (J/g K)**	=R[-1]C/calj
54		
55	**Cisf (cal/g K)**	=ai*Tsf+bi
56	**Cisf (J/g K)**	=R[-1]C/calj
57		
58	**basic [E] Numerator**	=(mo+E)*Coif*(Tf-Ti)-hot*(ms*Cizf*(Tz-Tf))-cold*(ms*Cisf*(Ts-Tf))
59		
60	**basic [E] Denominator**	=ms*(L+hot*(Cwsz*(Ts-Tz))-cold*(Cisf*(Ts-Tf))+cold*(Cizf*(Tz-Tf)))
61		
62	**Grav. Liquid Water Content:**	**=(Anum/Aden)**
63		
64	ΔT (K) =	=Tf-Ti
65		
66	**Snow Temperature (°C) =**	=TsC
67		
68	**Snow Density (g/cm^3) =**	not available
69		
70	**Vol. Liquid Water Content :**	**=GLWC*rhos**

	6	7
3	**Calories in a joule**	0.23901
4	**Freezing point of water (K)**	273.15
5	**Calorimeter Constant (g oil)**	80.344
6	**Latent Heat of Fusion of Water (J/g)**	333.458851

	10	11	12
2		Heat Capacities: Constants for linear appxn. (C=ax+b)	
3		**a**	**b**
4	**Ice (cal/g K):**	0.0019	-0.0082
5	**Water (cal/g K):**	-0.0006038	1.1719
6	**Oil (J/g K):**	0.0011998	1.1871

Calorimeter Measurement Program for HP-41CX

	1	2
1	LBL "TEMP"	*Calorimeter Program for HP41CX, Version of 28 January 1989.*
2	FIX 5	Fix display of HP41CX to five digits after decimal point.
3	AUTOIO	Set HP-IL to auto mode.
4	"HP3468A"	
5	FINDID	Find HP-IL address of digital multimeter.
6	SELECT	Select digital multimeter as primary device.
7	REMOTE	Set digital multimeter to remote mode.
8	"N5"	
9	OUTA	Set display of multimeter to 5 digits.
10	"F4"	
11	OUTA	Set multimeter to 4-wire ohm measurement.
12	"----------"	
13	ACA	
14	"----------"	
15	ACA	
16	"--"	
17	ACA	
18	PRBUF	Print dividing line at beginning of run.
19	RCLFLAG	
20	STO 11	Store all flag settings in register 11.
21	0	
22	ENTER^	
23	0	
24	BLDSPEC	
25	0	
26	BLDSPEC	
27	6	
28	BLDSPEC	
29	9	
30	BLDSPEC	
31	9	
32	BLDSPEC	
33	6	
34	BLDSPEC	
35	0	
36	BLDSPEC	
37	0	
38	BLDSPEC	"Build" special character (degree sign "°") for printer.
39	STO 12	Store "°" in register 12.
40	CLA	Clear Alpha register.
41	8	
42	XTOA	
43	ASTO 10	Store "Δ" character in register 10.
44	CLA	
45	40	
46	XTOA	Clear Alpha register.
47	ASTO 13	Store "(" character in register 13.
48	CLA	
49	41	
50	XTOA	Clear Alpha register.

	1	2
51	ASTO 14	Store ")" character in register 14.
52	CF 00	
53	SF 01	Set flag indicating 1st measurement (no ΔT wanted).
54	CF 02	
55	CF 03	
56	CF 04	
57	SF 27	Activate user keyboard.
58	STOPSW	Stop stopwatch.
59	0	
60	SETSW	Set stopwatch to zero.
61	"EMPTY MASS?"	
62	PROMPT	Prompt for mass of empty calorimeter.
63	STO 06	Store empty mass in register 6.
64	"MASS W/OIL?"	
65	PROMPT	Prompt for mass of calorimeter + oil.
66	STO 07	Store in register 7.
67	"R/S TO BEGIN"	
68	PROMPT	Prompt user to press R/S to begin measurement sequence.
69	TIME	Recall time to X register.
70	RUNSW	Start stopwatch.
71	STO 01	Store start time in register 1.
72	CLA	Clear alpha register.
73	DATE	Recall date to X register.
74	ADATE	Append date to alpha register.
75	PRA	Print date from alpha register.
76	CLA	Clear alpha register.
77	RCL 01	Recall start time from register 1.
78	FIX 4	Change to #.#### format (time will print as HH:MM:SS).
79	ATIME24	Recall start time to alpha register in 24-hour format.
80	FIX 5	Change to #.##### format.
81	PRA	Print start time from alpha register.
82	ADV	Advance printer one line.
83	"^^MEAS"	Store name of control alarm (which measures cal. temp).
84	0.0015	
85	ENTER^	Enter repeat interval for control alarm (15 sec.)
86	0	
87	ENTER^	Enter date for control alarm (0 = today)
88	RCL 01	Recall start time from register 1.
89	0.0015	
90	HMS+	Add 15 seconds to start time.
91	XYZALM	Set control alarm for 15 sec. from start time.
92	LBL 00	
93	"<A> TO ADD"	
94	CF 21	Clear printer enable flag.
95	AVIEW	Prompt user to press A when ready to add snow.
96	SF 21	Set printer enable flag.
97	LBL 01	
98	0.2	
99	GETKEYX	Return code of pressed key after 0.2 sec.
100	RDN	Put key code in X register.

	1	2
101	11	
102	X≠Y?	Was pressed key not the A key?
103	GTO 01	YES: Get another key code.
104	CLRALMS	NO: Clear the control alarm, stopping the 15 sec. meas.
105	BEEP	Sound a four-tone sequence.
106	"SNOW TEMP? C"	
107	PROMPT	Prompt user for snow temperature in °C.
108	STO 04	Store snow temperature in register 4.
109	"R/S WHEN ADD."	
110	PROMPT	Prompt user to press R/S when snow is added to calorimeter.
111	RCLSW	Get elapsed time when snow added.
112	STO 03	Store elapsed time in register 3.
113	ADV	
114	ADV	Advance printer 2 lines.
115	"SAMPLE ADDED AT"	
116	PRA	Print alpha register.
117	CLA	Clear alpha register.
118	FIX 5	Change to #.##### format.
119	ATIME24	Append elapsed time to alpha register in HH:MM:SS.s format.
120	PRA	Print elapsed time.
121	HR	Change elapsed time to decimal hours.
122	3600	
123	*	Convert elapsed time to seconds.
124	FIX 1	Change to #.# format.
125	CLA	Clear alpha register.
126	ARCL X	Append elapsed time to alpha register in #.# format.
127	"¬ "	Append space to alpha register.
128	ACA	Put alpha register in printer buffer.
129	115	
130	ACCHR	Append "s" to printer buffer.
131	PRBUF	Print printer buffer.
132	FIX 5	Change to #.##### format.
133	ADV	
134	ADV	Advance printer 2 lines.
135	TIME	Put current time in X register.
136	RCL 01	Recall start time.
137	HMS-	Subtract start time from current time.
138	HR	Convert time difference to decimal hours.
139	240	
140	*	Convert time difference to quarter minutes.
141	2	
142	+	Add a half minute (2 quarter minutes).
143	INT	Truncate decimal part to give integer number of quarter mins.
144	240	
145	/	Convert result back to decimal hours.
146	HMS	Convert to hours, minutes, seconds.
147	RCL 01	
148	HMS+	Add to start time. (Next meas. will be N*15 sec from start.)
149	0.0015	
150	X<>Y	Put repeat interval in Y register (15 sec.)

	1	2
151	0	
152	X<>Y	Put date in Y register (0 = today).
153	"^^MEAS"	Put name of control alarm in alpha register.
154	XYZALM	Set control alarm.
155	"<A> TO STOP"	
156	CF 21	Clear printer enable flag.
157	AVIEW	Prompt user to press A when ready to stop.
158	SF 21	Set printer enable flag.
159	SF 01	Set flag indicating 1st measurement (no ΔT wanted).
160	LBL 08	
161	0.2	
162	GETKEYX	Return code of pressed key after 0.2 sec.
163	RDN	Put key code in X register.
164	11	
165	X≠Y?	Was pressed key not the A key?
166	GTO 08	YES: Get another key code.
167	CLRALMS	NO: Clear the control alarm, stopping the 15 sec. meas.
168	BEEP	Sound a four-tone sequence.
169	"TOTAL MASS?"	
170	PROMPT	Prompt user for total mass of calorimeter, oil, & snow.
171	RCL 07	
172	-	Subtract mass of calorimeter + oil.
173	" M"	
174	ARCL 13	
175	"¬SNOW"	
176	ARCL 14	
177	"¬="	Put " M(SNOW) = " in alpha register.
178	FIX 2	Change to #.## format.
179	ARCL X	Append X register to alpha register.
180	ACA	Put alpha register in printer buffer.
181	32	
182	ACCHR	Append " " to printer buffer.
183	103	
184	ACHR	Append "g" to printer buffer.
185	PRBUF	Print contents of printer buffer.
186	RCL 07	
187	RCL 06	
188	-	Subtract mass of calorimeter from mass of calorimeter + oil.
189	"M"	
190	ARCL 13	
191	"¬FRZ AGT"	
192	ARCL 14	
193	"¬="	Put "M(FRZ AGT) = " in alpha register.
194	ARCL X	Append X register to alpha register.
195	ACA	Put alpha register in printer buffer.
196	32	
197	ACCHR	Append " " to printer buffer.
198	103	
199	ACCHR	Append "g" to printer buffer.
200	PRBUF	Print contents of printer buffer.

	1	2
201	"T"	
202	ARCL 13	
203	"¬ SNOW"	
204	ARCL 14	
205	"¬ = "	Put "T(SNOW) = " in alpha register.
206	FIX 1	Change to #.# format.
207	ARCL 04	Append snow temperature to alpha register.
208	"¬ "	Append " " to alpha register.
209	ACA	Put alpha register in printer buffer.
210	RCL 12	
211	ACSPEC	Append "°" to printer buffer.
212	"C"	
213	ACA	Append "C" to printer buffer.
214	PRBUF	Print contents of printer buffer.
215	" ="	Put " = " in alpha register.
216	273.15	
217	ST+ 04	Convert snow temperature from °C to K.
218	ARCL 04	Append snow temperature (K) to alpha register.
219	"¬ K"	Append " K" to alpha register.
220	PRA	Print alpha register.
221	RCL 11	
222	STOFLAG	Reset flags to original status.
223	STOPSW	Stop stopwatch.
224	0	
225	SETSW	Set stopwatch to zero.
226	LOCAL	Set digital multimeter to local mode.
227	CLX	Clear X register.
228	ADV	
229	ADV	
230	ADV	
231	ADV	
232	ADV	Advance printer 5 lines.
233	END	

	1	2
1	LBL "MEAS"	*Measurement Subroutine for HP41CX, Version of 28 January 1989.*
2	RCLSW	
3	STO 05	Store current elapsed time in register 5.
4	IND	Input resistance value from digital multimeter.
5	TONE 7	Sound a tone.
6	R^	
7	STO 22	Save Y register upon entry to subroutine in register 22.
8	R^	
9	STO 21	Save X register upon entry to subroutine in register 21.
10	R^	
11	R^	Restore resistance and time to X and Y registers.
12	STO 15	Store resistance in register 15.
13	ENTER^	
14	ENTER^	Duplicate resistance to Y and Z registers.
15	.9902136 E-3	
16	*	
17	2.360577	
18	+	
19	*	
20	27.19057	
21	+	Use 2nd degree polynomial to convert resistance to temp.
22	STO 18	Store temperature (K) in register 18.
23	273.15	
24	-	Convert to °C.
25	STO 17	Store temperature (°C) in register 17.
26	RCL 18	
27	RCL 19	
28	-	Calculate difference between current and previous temps, ΔT.
29	STO 20	Store ΔT in register 20.
30	RCL 18	
31	STO 19	Store current temp. as previous temp. in register 19.
32	RCL 05	Recall time of measurement.
33	CLA	Clear alpha register.
34	FIX 4	Change to #.#### format.
35	ATIME24	Place time of measurement in alpha register in HH:MM:SS fmt.
36	PRA	Print alpha register.
37	HR	Convert time of measurement to decimal hours.
38	3600	
39	*	Convert time of measurement to seconds.
40	FIX 0	Change to #. format
41	CLA	Clear alpha register.
42	ARCL X	Place time of measurement in alpha register (in seconds).
43	"¬"	Append " " to alpha register.
44	ACA	Put alpha register in printer buffer.
45	115	
46	ACCHR	Append "s" to printer buffer.
47	PRBUF	Print contents of printer buffer.
48	FIX 3	Change to #.### format.
49	"R = "	Put "R = " in alpha register.
50	ARCL 15	Append resistance value to alpha register in #.### format.

	1	2
51	"¬ "	Append " " to alpha register.
52	ACA	Put alpha register in printer buffer.
53	17	
54	ACCHR	Append "Ω" to printer buffer.
55	PRBUF	Print contents of printer buffer.
56	FIX 2	Change to #.## format.
57	"T = "	Put "T = " in alpha register.
58	ARCL 17	Append temperature (°C) to alpha register.
59	"¬ "	Append " " to alpha register.
60	ACA	Put alpha register in printer buffer.
61	RCL 12	
62	ACSPEC	Append "°" to printer buffer.
63	"C"	
64	ACA	Append "C" to printer buffer.
65	PRBUF	Print contents of printer buffer.
66	" = "	Put " = " in alpha register.
67	ARCL 18	Append temperature (K) to alpha register.
68	"¬ K"	Append " K" to alpha register.
69	PRA	Print alpha register.
70	CLA	Clear alpha register.
71	FIX 2	Change to #.## format.
72	ARCL 10	Put "Δ" in alpha register.
73	"¬T = "	Append "T = " to alpha register.
74	ARCL 20	Append ΔT to alpha register.
75	"¬ K"	Append " K" to alpha register.
76	FC?C 01	Is this not the first measurement? Clear the flag if set.
77	PRA	YES: Print alpha register (containing ΔT)
78	ADV	Advance paper 1 line.
79	RCL 22	
80	RCL 21	Restore original X and Y registers.
81	END	

Memory Map for Calorimeter Program

MEMORY MAP

Register	Contents (Italicized entries are used in MEAS.)
0	
1	Start time.
2	
3	Elapsed time when snow added.
4	Snow temperature, °C
5	*Current elapsed time (time of measurement).*
6	Empty mass.
7	Mass of calorimeter + oil.
8	
9	
10	Delta "Δ"
11	Flag$
12	Degree Sign "°"
13	"("
14	")"
15	*Resistance value measured by multimeter*
16	
17	*Measured temperature (°C)*
18	*Measured temperature (K)*
19	*Previous value of measured temperature (K).*
20	*ΔT (Tcurrent-Tprevious)*
21	*X register upon entry to MEAS routine*
22	*Y register upon entry to MEAS routine*