LINEAR, HIGH PRECISION, REDUNDANT CALORIMETER

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Abstract

Criticisms of the calorimetry have often provided the basis for challenges to reports of observations of excess heat in metal hydride and metal deuteride systems. This report describes calorimeters which are immune to most such challenges. In this paper, the design objectives are elucidated, the design features of the calorimeter are modeled, the calibration results are shown, and data from the operation of control cells are given.

Introduction

Claims of excess heat from "cold fusion," i.e. heat beyond the limits obtainable by chemical or mechanical processes, have frequently been challenged because of purported calorimetry problems. Open cell calorimetry has been challenged with special severity: some systems have changing calorimetric "constants"; others leave open questions about whether all of these gases were removed as assumed, i.e. with no recombination. In addition, due to a significant amount of the heat being transferred by radiation and convection, the calibration curves are often far from linear, requiring extensive modeling and analysis to interpret the results of live runs.

To solve these problems, we are running closed electrolytic cells (using an internal recombiner) inside calorimeters having the following characteristics: (1) high precision from 200 mW to 20 W of power; (2) linear output for ease of interpretation; (3) redundancy in the heat measurement; (4) long term stability; (5) independence of the heat source position within a cell; (6) a reasonably short time constant, allowing the structure of heat bursts to be seen.

The basic design includes inner and outer shells of Al or Cu, connected by a large number of thermoelectric modules (TEMs) wired in series. Utilizing the Peltier effect, these modules produce an output voltage proportional to a temperature difference across their faces; the temperature difference is, in turn, proportional to the heat flow through the modules. Arranged so that nearly all of the heat flows through TEMs with output terminals wired in series, the calorimeter gives a response very nearly proportional to the net heat flow through the calorimeter. (In the ideal case, none of the heat would flow by radiation or convection, causing the response to be as linear as the TEMs or Peltier elements themselves.)
Figure 1 shows a schematic of the design, with an inner chamber of length of 16.5 cm, diameter 3.81 cm, and outer dimensions of length 25.4 cm, diameter 8.89 cm. Since flat, square TEMs are commercially available, assembly is simplified if the inner block has a square cross section, with a round hole for the cell, and the TEMs are held on by Al "fins," using heat sink compound to improve conductivity. The fins are turned in a lathe and inserted into the outer shell with 0.13 mm radial clearance, enough that when the inner block is much hotter, the air gap will not be eliminated, thus protecting the TEMs from being crushed.

The inner and outer lids are secured with screws and heat sink compound, for good thermal contact. The inner lid is capped with 2.5 cm of styrofoam, with two layers of Al foil, to reduce radiation and convection. All wires used are #30 Cu, except two (between the lids) of stranded #24 Cu. These wires are thermally connected to the lids to provide a reproducible heat loss path.

Between the inner block and the fins, the spaces to the sides of the T' Xxs have two thin layers of mylar, to obstruct air movement and aid in assembly.

Temperature sensors are Pt resistance temperature devices or RTDs (1000 ohms at 0°C). T1 through T4 are inserted into holes in the cell lid and inner block. Sensors T5 and T6 are cemented into a groove on the inner wall of the outer shell. These sensors monitor the cell and provide the backup isoperibolic calorimetry. Heat flow is closely proportional to the temperature difference between inner and outer shells.

The constant temperature water bath has a 5 cm thick foam lid, sealed at the edges to prevent loss of water vapor. Four round holes allow four calorimeters to be suspended in the bath by a flange provided near the top of each calorimeter such that a good water vapor seal is obtained. This provides better temperature stability and keeps electrical connections dry. An additional 5 cm of foam covers the tops of the calorimeters and cable leads.

Modeling the Calorimeter

Heat flow by conduction is given by $H = \Delta T/R$, where $\Delta T$ is the temperature difference and $R$ is the thermal resistance. $R$ is given by $R = \Delta x/kA$, where $\Delta x$ is the thickness, $A$ the cross sectional area, and $k$ the thermal conductivity. In this formulation, combinations of serial
and parallel heat paths may be treated like combinations of electrical resistors in series and parallel.

Where radiation and/or convection contribute a small part, these can also be formulated as parallel thermal resistances. Radiative heat flow is \( H = a_\sigma A(T_2^4 - T_1^4) \approx 4a_\sigma A^3 \Delta T \), giving \( R = 1/4a_\sigma A^3 \), where \( \sigma = 5.672 \times 10^{-8} \text{ W/m}^2\text{K}^4 \), and \( a_\sigma \approx 0.1 \) for aluminum. Convective losses can be treated with \( R = 1/Ab \Delta T^4 \), where \( b = 2.49 \text{ W/m}^2\text{K}^{3/4} \) for the top of the warm lid, \( b = 1.77 \text{ W/m}^2\text{K}^{3/4} \) for a wall surface, and \( b = 1.31 \text{ W/m}^2\text{K}^{3/4} \) for a bottom surface.

Using these expressions, the thermal resistances of the various areas can be calculated, using \( \Delta T = 6^\circ \text{C} \) (approximately true for 20 watts), and \( T = 63^\circ \text{C} = 336 \text{K} \).

The thermal resistance across the inner Al block to the TEMs is a negligible \( R \approx 0.003 \text{ K/W} \), using \( \Delta x = 1.5 \text{ cm} \), \( A = 250 \text{ cm}^2 \), and \( k = 205 \text{ W/mK} \). Across the outer Cu block the resistance is smaller still. Thus each block is at a uniform temperature, \( T_1 \) (inner block) or \( T_2 \) (bath).

The main heat path is expected to be through the TEMs. A measured value for one module (Melcor type CP-1.4-127-045L-2) is 2.78 \( \text{^\circ C/W} \). The heat sink compound has \( k = 0.215 \text{ W/mK} \), \( A = 16 \text{ cm}^2 \), \( \Delta x = 2.5 \times 10^3 \text{ cm} \) (including both layers), giving \( R = 0.073 \text{ K/W} \). The total resistance for a TEM plus the compound, divided by 12, gives the resistance through the TEM path as \( R_{\text{TEM}} = 0.238 \text{ K/W} \).

The areas at the sides of the TEMs gives a parallel resistance \( R_p \), as indicated in Fig. 2. With \( A = 156 \text{ cm}^2 \), \( \Delta x = 0.33 \text{ cm} \), and \( k \approx 0.03 \text{ W/mK} \), this air conduction gives \( R = 8.6 \text{ K/W} \). Convection is broken into three parts by the two layers of mylar. If each has \( \Delta T/3 \) temperature difference and two walls, the convective resistance is 217 K/W. Radiative resistance (assuming mylar is transparent to IR) is 74.5 K/W. Another side path is through the screws. These are stainless steel with a nylon washer to prevent metal-to-metal contact (and two Belville washers, which provide spring action to prevent crushing of the TEMs). The resistance through the 32 screws and washers is estimated to be 5.1 K/W. Combining these four resistances gives \( R_s = 3.05 \text{ K/W} \).

Using circuit theory, one sees that of the heat passing through the fins and air to the outer shell, 7.3% passes around the sides of the TEMs.

\[ \text{Figure 2 Thermal resistance network.} \]

Heat from the cell (or, alternatively, from the inner block) travels primarily through the TEM path, then through the fins and air gap to the outer shell which is at bath temperature.

\[ \text{21-3} \]
The resistance through the fins (using $\Delta x = 0.8 \text{ cm}$, $A = 361 \text{ cm}^2$) is 0.001 K/W, and conduction through the air gap ($\Delta x = 0.013 \text{ cm}$, $A = 370 \text{ cm}^2$) is 0.140 K/W.

Heat paths directly from inner to outer shells include: wire leads, lid losses, base losses and corner losses. These four in parallel constitute $R_D$. Three of these include radiation and convection losses. Resistance through the wires (two #24, five #30, all 10 cm long) is 391 K/W. The equivalent resistance of the lid, base, and corners is 29.6 K/W, giving $R_D = 25.8$ K/W.

Combining all resistances, the total equivalent resistance is $R_{\text{eq}} = 0.36$ K/W. Of the total heat flow, 91% flows through the TEMs. Radiative paths carry 0.51% of the heat and convective paths 0.46%, such that only 0.97% is non-conductive. Non-linearities should thus be less than 1%, especially at less than 20 W power. At 20 W, $\Delta T$ should be $\Delta T = RH = 7.2^\circ \text{C}$, near the 6K assumed for the calculations.

The time constant is given by $T = (\Sigma mc)R$, where $\Sigma mc$ is the sum of mass times heat capacity, assuming the thermal mass is all in the inner block. The thermal capacity of the cell plus the inner block is 995 J/K, which with the total resistance $R_{\text{eq}} = 0.36$ K/W gives a reasonably short time constant of $\tau = 6.0$ minutes.

According to the above calculations, does this calorimeter meet all the criteria in the introduction?

The precision will depend on measurement electronics and on the effect of variations in room temperature. Certainly the output should be acceptably close to linear.

The backup system uses RTDs calibrated by the supplier to $\pm 0.1^\circ \text{C}$, but capable of in-situ calibration to $\pm 0.01^\circ \text{C}$ or better. If 20 W gives $\Delta T = 7.2$ K, an error of $\pm 0.01^\circ \text{C}$ is equivalent to about $\pm 30$ mW. This will be compared with actual performance, but should provide acceptable redundancy for thermal power measurements. In addition the inner and outer temperatures have at least two RTDs each, guarding against failure of a single component.

The components used are expected to have long-term stability, as would any closed cell operating normally. Position of the heat source in the calorimeter should not change the output significantly. This will be tested with two separate calibrations. Finally, the time constant is short compared with many of the heat bursts reported by others.

**Calibration**

The behavior of the calorimeter can be modelled accurately with the equation

\[ P = m_1 C_o + m_2 C_o (T - T_e) + b_1 + b_2 (T - T_L) \]

where $m_1$, $m_2$, $b_1$, and $b_2$ are calibration constants, $C_o$ is the output voltage of the calorimeter, $T$ is the bath temperature, $T_e$ is an arbitrary fixed bath temperature ($60^\circ \text{C}$ in this work), and
\( T_L \) is the laboratory temperature. The first term, \( m_1 \), \( C_o \), which represents the linear output of the TEMs dominates, while the other terms represent small corrections. The second term represents a possible tiny temperature dependence of the TEMs plus other unknown effects. The last two terms represent small amounts of heat flow from the bath to the laboratory through the TEMs; the entire bath-calorimeter system is well insulated with the result that these terms are small, but they are dependent on the position of the calorimeter within the bath.

The calorimeters were calibrated with resistance heaters placed in two different positions: the first is in a metal cell placed in the cell cavity; the second is in a hole in the inner calorimeter block. The power input varied between 49 mW and 20 W, while bath temperatures varied between 40\(^\circ\)C and 75\(^\circ\)C. Measurements were begun 90 minutes after each power and bath temperature setting. Every five minutes, the average value of 10,000 measurements of \( C_o \) was recorded for each calorimeter.

The parameters in equation (1) were fit to the data taken with a heater inside a metal cell. The results are:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Calorimeter #1</th>
<th>Calorimeter #1</th>
<th>Calorimeter #1</th>
<th>Calorimeter #1</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m_1 )</td>
<td>14.237</td>
<td>14.434</td>
<td>14.323</td>
<td>14.638</td>
</tr>
<tr>
<td>( m_2 )</td>
<td>-0.00363</td>
<td>-0.00581</td>
<td>-0.00927</td>
<td>-0.0125</td>
</tr>
<tr>
<td>( b_1 )</td>
<td>0.0239</td>
<td>0.0139</td>
<td>-0.0007</td>
<td>0.0007</td>
</tr>
<tr>
<td>( b_2 )</td>
<td>-0.00026</td>
<td>-0.00013</td>
<td>0.00019</td>
<td>0.00046</td>
</tr>
</tbody>
</table>

When these parameters (taken with heaters in metal cells) were used to calculate the heat flow from resistors in the inner calorimeter block, the calculations differed with the measured power input by a standard deviation of only 1.6 mW averaged over the four cells. With such a difference between the calibration heater position and the heater position of these measurements, the agreement suggests both a high degree of precision of the heat measurement and of position independence for the heat source. (In actual use, the heat source will always be positioned inside a metal cell.) The graph at right shows calibration and comparison data over an extended power input range for one calorimeter. The graphs on the next two pages show similar data for a more restricted power input range for all four calorimeters; the restricted range makes it easier to distinguish the data from the two heat source positions.
Cell Data

The figure at the right shows data taken over a 54-day period with two cells in two of the calorimeters described above. One cell was a control cell with a silver cathode; the other had a palladium-boron alloy cathode (0.3 atom% boron). The two are very nearly equivalent. However, the loading in the Pd-B cathode was not well known; it had a d/Pd atom ratio of about 0.8. The final excess power settled at within ± 0.5 mW of zero (about 0.025%).

Conclusion

The calorimeters appear to meet or exceed the original design criteria for accuracy, precision, linearity, simplicity of output interpretation, and reliability.

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Figure 7 Data from two cells, a silver-cathode control cell and a palladium-boron alloy cathode. Because loading in the Pd-B cathode probably did not exceed 0.8, no excess heat was expected. Input power was about 2 watts.