Introduction to Calorimetry

The production of power and heat energy is the first, most studied, and some would say, the most important, activity for the experimental study of LENR. It requires that the energy source be within a calorimeter, which gives the power flowing into and out of the vessel containing the source, and hence, the net power and energy. Because of their importance to the study of LENR, calorimeters were featured during ICCF-14. It is noted in passing there has been some calorimetry done in experiments involving gas, plasma and beam loading of materials with hydrogen isotopes. However, most LENR calorimetry has been done with electrochemical loading, and that is our focus. This section provides some basic information on calorimeters and introduces the papers on the following pages.

In most LENR experiments, the ultimate goal is to measure net power (output minus input) as a function of time. Integration of the net power-time curve gives the net energy produced. In one type of calorimeter based on melting ice, the net energy is obtained directly without having power as an intermediate value. The ice calorimeter is a so-called "first principles" calorimeter since the heat of formation of ice is well established and does not depend upon calibration of the device, just accurate weight and volume measurements.

A calorimeter is, most fundamentally, a measurement instrument. Like most measuring devices, it requires a calibration curve, which relates the value that is wanted to the signal provided by the instrument. This curve is sometimes called an "instrument function." Calibration curves almost always have three regions, (a) a lowest signal value due to some kind of noise, (b) a range of usefulness (the dynamic range) and (c) a region where the output no longer increases or saturates for some reason. In the case of LENR experiments, the power at any time is what is needed from a calorimeter. The noise largely determines the minimum value of power that can be reliably measured. The signals from LENR calorimeters are generally voltages, but can also electrical currents or weights.

Like all sensors and measuring instruments, some fundamental mechanisms are behind the operation of LENR calorimeters. There are two primary mechanisms of interest here. The first is the heating of some material, commonly a liquid electrolyte, in which the energy source is immersed. The relevant equation is $(\Delta H/\Delta t) = M\ C_p\ (\Delta T/\Delta t)$, where H is the heat energy, M the mass of the material heated, C_p the heat capacity, ΔT temperature rise of the material and t is time. This equation shows that, when M and C_p are known, measurement of $(\Delta T/\Delta t)$ will give the thermal power $(\Delta H/\Delta t)$ produced at some time. The second mechanism is thermal conductivity through some barrier to the escape of heat from the region of the source. It is governed by the equation, $(\Delta H/\Delta t) = KA(\Delta T/\Delta x)$, through area A in the x direction, where K is the thermal conductivity. Some LENR calorimeters work on the basis of heating of a material and others by heat conductivity. They will be noted below.

In general, the production and flow of heat in thermal science is closely analogous to the motion of electrons or photons. In all three cases, there are sources, intermediate objects and sinks. In electronics, a source of electrons (such as a battery) sends current to active or passive devices (for example, transistors and resistors) and ultimately to ground. In optics, sources (such as light emitting diodes) send photons through optical devices (notably, lenses) to absorbers. For LENR power measurements, the source of interest is the region in which the nuclear reactions occur and produce energy, the intermediate objects are thermal barriers and the sink is ultimately the surrounding environment. In electronics and optics, there are usually sources of currents or light that compete with the process of interest. This is also true of thermal measurements, including calorimetry for measuring the effects of LENR.

All three types of heat transfer are relevant: conductive, convective and radiative. There can be desirable and undesirable additions or losses of heat to and from the cell in a calorimeter, as summarized in the following table. It is assumed that the cell is at a higher temperature than its surroundings, that is, heat flows from the cell into nearby matter.

	Addition of Energy	**Loss of Energy**
Wanted	LENR Calibration Heater	Conduction via the Desired Path
Unwanted	Chemical Reactions Electrochemical Reactions Warm makeup electrolyte	Conduction by Other Paths IR Radiation Gas Escape or PV Work

Several types of calorimeters have been used in LENR experiments. Isoperibolic calorimeters were used by Fleischmann and Pons, and many other researchers. They have constant temperatures in their surrounding regions (termed “jackets”) in contrast to isothermal calorimeters, for which an auxiliary system maintains the heat-producing cell at a constant temperature over time. There are different configurations for isoperibolic calorimeters. In one, the temperature difference between the cell and jacket is measured. This arrangement sometimes suffers from problems with the non-uniform distribution of temperatures within the cell, and spatial differences between a cathode producing LENR and a nearby calibration heater. In another configuration, there is a second wall between the jacket immediately around the cell and the surroundings. In this case, the temperature difference is measured between the two regions outside of the cell. It is insensitive to temperature variations within the cell due to any cause. Both of these configurations have temperature measurements made at a few specific locations within the liquids of the cell, the jacket region or the outer water bath. Thermisters or thermocouples are commonly used for the temperature determinations.

Another variation of the isoperibolic calorimeter is termed the Seebeck calorimeter. In this case, many thermocouples are used to measure the temperature drop due to heat conductivity between the inside and outside of a thermal barrier containing the cell. This arrangement is also insensitive to details of the temperature distributions within the cell and, because the voltage-producing thermocouples are connected in series, larger signals can be obtained. Recent widespread availability of Peltier devices has made them a popular choice to replace the thermocouples in Seebeck calorimeters.

Another type of calorimeter is described as “mass flow.” Here, a liquid, commonly water at a known temperature flows into the vicinity of the cell, acquiring heat and increasing in temperature. Measurement of the output temperature, that is, the temperature increase, and the flow rate, gotten by weighing, gives the measure of power production. The "heat flow" calorimeter, like the ice calorimeter, is a "first principles" device.

The above types of calorimeters have been the main instruments used in LENR heat-production experiments. However, other calorimeter types have also been employed. One of them is called a "heat flow" instrument. There are essentially four constant temperature regions in this kind of calorimeter. They include the following, from the outside to the interior cell. The outer region is a constant temperature bath. The second is a metal heat sink maintained at a constant temperature with a feedback system. It is connected to a region surrounding the cell by another metal piece that serves as a heat leak from the third region to the metal plate (and contains the electrical leads). The third region contains the fourth, the electrolytic cell. The cell and surrounding region are maintained at a constant temperature by an electrical heater driven by a current. Hence, the output signal from this type of calorimeter is the current, that is, the power that must be supplied to maintain the interior temperature. If heat is produced in this isothermal calorimeter, less current is needed. The principle behind this instrument is widely applied in engineering: feedback is used to keep a system near its unchanged condition, with the feedback signal being the output. It permits very sensitive measurements over a wide dynamic range.

The last kind of LENR calorimeter is also very different from the isoperibolic, Seebeck and mass flow instruments that have been most widely used. It is an "ice calorimeter." Heat produced in an electrochemical cell is coupled into a surrounding ice and water mixture, melting some of the ice. The approximately 9% decrease in volume when ice melts is transferred to a container of liquid mercury. The difference in that volume is obtained by weighing the mercury volume change. The denser mercury permits more precise weight determinations.

A tabular summary of main features of the different types of LENR calorimeters follows.

	Isoperibolic			**Mass Flow**	**Heat Flow**	**Ice**
	Single Wall	**Double Wall**	**Seebeck**			
Principle Mechanism	Heat Conductivity	Heat Conductivity	Heat Conductivity	Heat Capacity	Heat Conductivity	Heat Capacity
Hotter Region	Cell electrolyte	Cell jacket	Inside of Barrier	Cell jacket	Metal Plate	Cell
Colder Region	Cell jacket	Outer bath	Outside of barrier	Flowing fluid	Cell and jacket	Ice-water
Measured	Power	Power	Power	Power	Power	Energy
Sensors	Temperature	Temperature	Temperature	Temperature & weight	Temperature	Weight
Signals	Voltage	Voltage	Voltage	Voltage	Voltage	Voltage

As noted, thermal sensors can be thermocouples, thermistors or Peltier devices. The voltage signals can be obtained in either analog or digital form, although acquisition, storage and manipulations of digital data are most common nowadays.

The characteristics, advantages and disadvantages of the different types of calorimeters vary widely. And, their design, construction, and operation also can be quite different even for one type of calorimeter. The same is true of their performance features. The features of the calibration curve for any calorimeter embodiment are central to the choice and use of a calorimeter for a specific experiment. They include the noise floor (for the combination of a calorimeter and its associated electronics), the sensitivity (the minimum power levels that can be measured adequately), the responsivity (slope of the calibration curve), and the dynamic range (in power or energy). Accuracy and precision are important for calorimeters, as for most measurement systems. The temporal response and the stability are other crucial parameters. The temperature range over which a calorimeter works is often important. Redundant measurements, ease of use, low cost and safety are other considerations. Cell size is an important consideration, which influences many of the performance and other characteristics.

In his presentation at ICCF-14, Storms gave the requirements for accurate calorimetry and sources of errors in measurements. The requirements for accuracy are constant temperatures for the ambient and reference media, controllable and constant applied power, stable measurement equipment, redundant measurements (with associated calibrations), and measurement of gas loss or gain. Errors in calorimetery, especially at low power (or heat) levels, can arise from inaccurate calibration curves, changes in ambient temperatures, variations in thermal conductivity, unknown recombination, electrical and other noise, and bubble action.

The papers in this section are arranged in the order discussed above. Miles and Fleischman presented details on the use of isoperibolic calorimeters in their invited review. Storms gave the invited paper on Seebeck calorimeters, and Zhang, Dash and Zhang provided a contributed paper on their new Seebeck instrument. McKubre and Tanzella, who have done over 100,000 hours of mass flow calorimetry, were invited to describe that kind of instrument. Little, Luce and Little described their version of a mass flow calorimeter. The heat flow calorimeter was presented in an invited paper by Lautzenhiser, Phelps and Eisner. Finally, the ice calorimeter was described in the invited paper by Dufour, Dufour, Murat and Foos.

This collection of review and recent papers on LENR calorimeters represents one of the best resources for study of these challenging and crucial instruments. If a person wants a primer on calorimeters for LENR, the 2004 paper by Storms is recommended. It is entitled “Calorimetry 101 for Cold Fusion: Methods, Problems and Errors,” and is available under Storms in the library at LENR-CANR.org (http://lenr-canr.org/acrobat/StormsEcalorimetr.pdf).

The overall situation on LENR calorimeters is now quite clear. Several types of calorimeters, and many variations of some of them, have been developed, calibrated and employed in hundreds of experiments. It has been demonstrated by calibrations, test measurements and live cell measurements, that many of the calorimeters used for LENR experiments can reliably measure powers of 100 mW and greater. Some have achieved sensitivities near 1 mW. The power levels from LENR experiments have often exceeded 1 W and sometimes tens of watts. Hence, there is no longer a question of having adequate signal-to-noise ratios. Some critics still assert that LENR experimenters are incapable of measuring input powers (energies) properly. However, that is not a problem, although better documentation of input power checks is desirable. In short, advances in calorimetry can be expected. However, if there were no further improvements, the calorimeters now available to the field would suffice. These include both "homemade" and commercial instruments.

There is also a class of calorimeter that uses identical devices but places the active experiment in one and a "blank" experiment in the other. The difference in output is attributed to the experiment and the noise from the environment can be cancelled by subtraction of the blank from the experimental chambers. These differential devices can be made to do high precision and stable heat measurements over wide dynamic ranges and for modest cost. It is expected that such instruments will be used increasingly in the study of LENR.