gSKIN® Application Note: Calorimetry

Direct and precise calorimetric measurements with the gSKIN® Sensor

The gSKIN® Heat Flux Sensor enables direct and highly precise measurements of reaction enthalpies in a variety of applications, including calorimetry. Calorimetric measurements are of paramount importance in the fields of chemical engineering, physical chemistry, materials science and biology.

Direct measurement
"Thanks to the heat flow based measurement, you do not need an isolated reaction chamber. For many measurements, you don't even need a thermometer."

Easy to use
"The small size and robust packaging allows for a simple application on virtually all surfaces."

Wide range of sample volumes
"Use the same sensor for the analysis of samples volumes ranging from cubic millimeters to cubic meters."

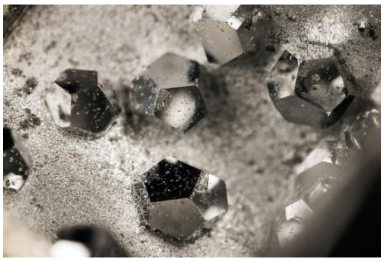
High sensitivity
"Measure heat energies of less than one millijoule on an assay of just one cm^3."

Applications

The fields of application of the gSKIN® Heat Flux Sensor are numerous and vast as the field of calorimetry itself. The small standardized sensors are ideal for measurements in research and development as well as in an educational context. In cooperation with manufacturers of chemical lab equipment, the gSKIN® Heat Flux Sensor can also be tailored and built in as an integral part of high-end chemical synthesis systems.

Process safety control
Calorimetric data is essential for process safety control. The heat release rate of novel chemical reactions must be known in order to design the cooling and heating systems for large scale synthesis. With the help of our sensing solutions, chemical engineers can provide this information already in the research lab while working on small reaction volumes.

Chemical engineering
In order to find the most productive chemical reactions, many different solution combinations must be tested. The direct reaction enthalpy measurement enables higher throughput and more reliable data in analytical research and diagnostic testing.



Material science
The engineering of energetic materials, such as phase change materials for latent heat energy storage, relies on precise calorimetric measurements. The same applies for many analytical techniques in materials science including the measurement of heat capacities or the investigation of microstructural changes.

Biology
Calorimetry is used for non-invasive measurements of metabolic activities in biological systems, from cell cultures up to athletes. Gain insights into the energy balance of living systems.

Education
Illustrate and explain the concepts of exergonic and endergonic reactions, enthalpy, heat capacity etc. with live measurements of the heat flows.

Measurement Setup

Figure 1 shows an example of a simple calorimetric measurement of a liquid solution using the gSKIN® Heat Flux Sensor. The individual parts of the setup and the measurement principle are described in the following paragraph.

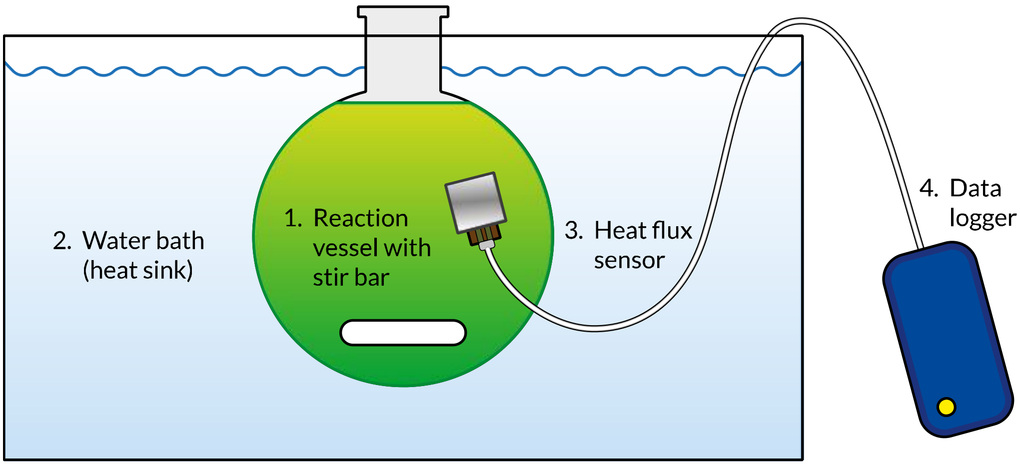


Figure 1: Simple calorimetric measurement setup for liquid solutions. The setup consists of a reaction vessel of Pyrex glass, a heat flux sensor and a water bath acting as a heat sink. The heat sink / water bath may be heated to the desired reaction temperature.

1. **Reaction vessel**
The total heat transfer through the reaction vessel is extrapolated from the local reading of the heat flux sensor. In order to get accurate results, the vessel needs to fulfill some requirements with respect to geometric and thermal uniformity:
    - In order to guarantee a uniform heat flux distribution, the shape of the vessel should be close to spherical. Cylindrical vessels work as well, due to their rotational symmetry. Cubic or prismatic vessels will only provide accurate results if you include a setup correction factor (see Appendix 1 for details). Avoid vessels with conical shape or complex geometries and recessions.
    - Avoid exceedingly thermally conductive or insulating vessel materials. Glassware with uniform wall thickness around 1mm will work best.

2. **Water bath / heat sink**
The heat generated during the reaction must be carried away by a heat sink in order to be measured by the sensor. Water will work well since it has a large heat capacity. Use at least 10x more water than the volume of your reaction vessel.

3. **gSKIN® Heat Flux Sensor**
gSKIN® Sensors transform the heat power flowing through the reaction vessel into an analog voltage. In most applications, the voltage signal is in the range of a few mV. Customization options are described in Appendix 3.

    Correct mounting of the sensor to the reaction vessel is of paramount importance for getting precise and reproducible measurements. Table 1 provides options for achieving good thermal integration of the sensor into your system.

Option	Description/Instruction
Double-sided adhesive tape	Adhesive tapes offer average thermal coupling and reasonable mechanical stability. The measurements may not be as reproducible as with other mounting methods. In return, the sensor can be repositioned at will and transferred to other surfaces.
Thermal paste	Thermal pastes offer good thermal contact when applied appropriately. Pastes are also suitable for filling up recessions or compensating for curvatures of the reaction vessel. The mechanical stability of such a bond however, is generally weak and requires special attention.
Thermally conductive epoxy adhesive	Thermoset adhesives offer the best performance with respect to mechanical stability and reproducibility of the measurements. However, this is a permanent bond and the sensor cannot be repositioned.
Silicone mold	More advanced permanent and repositionable sensing solutions can be designed with elastomeric molds.

Table 1: Mounting options for the gSKIN® Heat Flux Sensor.

4. **Read-out electronics**
The output signal of gSKIN® Heat Flux Sensors is an analog voltage response. If the analog input of your read-out electronics has a resolution of 1 µV, you can directly record the output signal.
greenTEG offers different electronic components to facilitate the read-out: In order to reach a signal in the mV range, a low-noise amplifier was developed. Furthermore, the analog signal can be digitalized to provide a digital interface. Contact us for further information.

The heat flux φ is proportional to the measured voltage U:

$$\varphi = U / So \qquad [W/m^2]$$

where φ is the heat flux in W/m2,
U is the output signal from the sensor in V,
So is the sensitivity of the gSKIN® Sensor in $\mu V/(W/m^2)$.

The sensitivity value So is obtained from calibration and provided by greenTEG for every sensor. For highest precision, we recommend to calibrate the sensor once it has been integrated into the system.

Working principle

In the absence of endothermic or exothermic reactions in the reaction vessel, the temperatures of the reaction vessel and of the heat sink are the same. There is no heat flow between the two reservoirs and therefore no signal is recorded.

As soon as heat energy is released or absorbed in the reaction vessel, there will be a net heat flow through the sensor. When the reaction ends and thermal equilibrium is reached, the heat flow will be equal to zero again.

The sensor output voltage U is proportional to the heat flux φ. The heat flux φ is measured in W/m^2. In order to get the amount of heat energy ΔE crossing the vessel surface, the heat flux must be multiplied by the measurement time Δt in seconds and by the outer surface A of the reaction vessel in square meters. A calibration constant So (in $\mu V/(W/m^2)$) is further needed to establish the proportionality between voltage and heat flux.

$$\Delta E = \varphi \cdot A \cdot \Delta t = (U / So) \cdot A \cdot \Delta t \qquad [J]$$

where ΔE is the energy change in J,
A is the vessel surface in m^2,
Δt is the measurement time in s.

Please refer to the document “gSKIN® Application Note: Molar Enthalpy of Salt Dissolution in Water” for a step-by-step tutorial of a simple calorimetric measurement of the molar enthalpy of salt dissolution in water.

greenTEG AG Technoparkstrasse 1
8005 Zürich, Switzerland
T: +41 44 632 04 20
F: +41 44 632 14 62
info@greenTEG.com
greenTEG.com

Appendix 1: Setup correction factor

Every sensor is carefully calibrated by greenTEG using a standard procedure. However, once the sensor is integrated into a custom setup, the sole calibration constant may not prove satisfactory due to the unique thermal boundary conditions of the system. These influences can be compensated by introducing a setup correction factor X_{corr}.
The correction factor of any self-made measurement setup can be easily derived with the help of hot water and a temperature sensor. The combined heat flux/temperature data logger provided by greenTEG (i.e. gSKIN® DLOG-4228) will work best for this task.

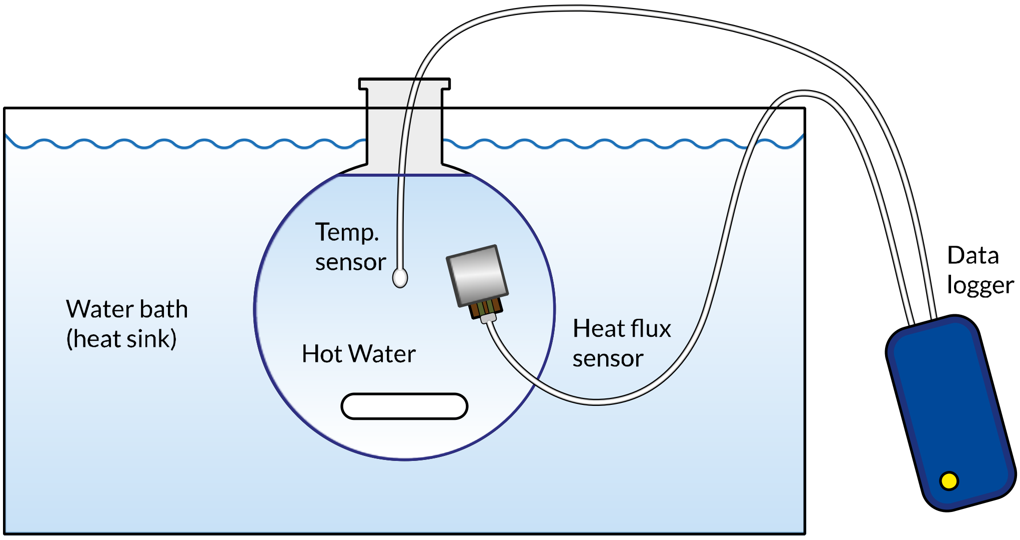


Figure 2: How to calibrate your system with hot water.

gSKIN® Heat Flux Sensor

To determine the correction factor X_{corr}, follow these steps:

1. Set up your experiment as shown in Figure 2.
2. Pour an exact amount of hot water into the reaction vessel. Choose water temperature slightly above your expected experimental conditions.
3. Wait 1 minute for the system to reach equilibrium.
4. Start data logger and record simultaneously both heat flux and water temperature until the water temperature has reached room temperature.
5. Select a temperature range ΔT that best represents your experimental conditions (e.g. cooling from 40°C - 30°C).
6. Calculate the energy change ΔE while the temperature was in the chosen temperature range (use the formulas on page 4). The document "gSKIN® Application Note: Molar Enthalpy of Salt Dissolution in Water" can serve as a practical example of this data analysis.
7. Divide the obtained energy ΔE by ΔT. This value corresponds to the measured heat capacity c_{pm} of water in this temperature range.

$$c_{pm} = \Delta E / \Delta T \qquad [J/K]$$

8. The correction factor X_{corr} is calculated by dividing the theoretical heat capacity c_{pt} by the measured heat capacity c_{pm}.

$X_{corr} = c_{pt} / c_{pm}$	[J/K]

9. Multiply all future measurement values by X_{corr} to correct these values.

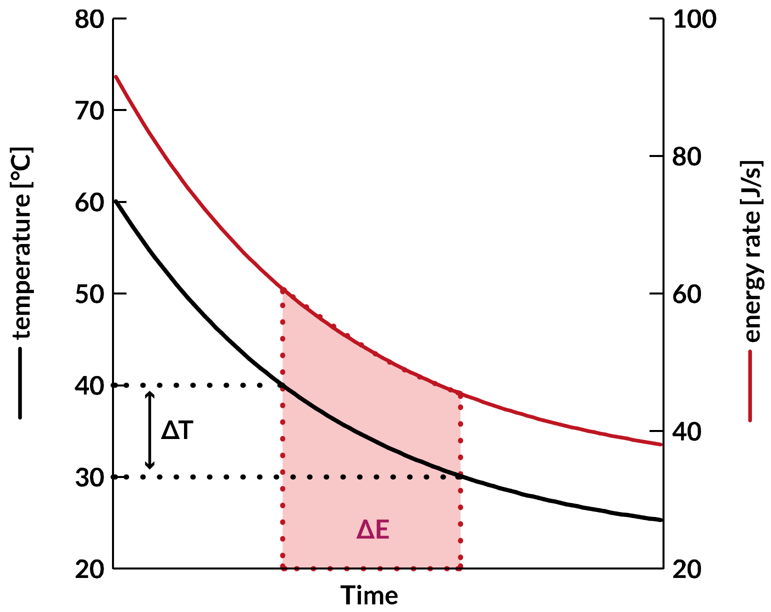


Figure 3: Schematic results of a calibration setup as described in the main text. As the water cools from 40°C to 30°C it releases heat energy. The amount of energy released during that time corresponds to the (known) heat capacity of water between 30°C and 40°C.

Appendix 2: Sensor specifications

greenTEG offers different standardized gSKIN® Heat Flux Sensors. All standardized sensors, including specifications and prices for single units are available at http://shop.greenteg.com/.

Appendix 3: Customization options

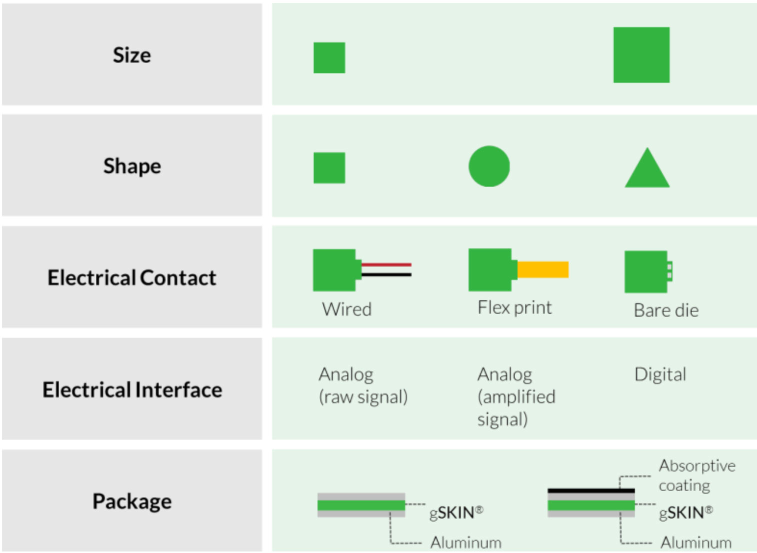


Figure 2: Customization options of size, shape, electrical contact, electrical interface and package. “Flex print” describes FFC/FPC options.

Document information

Pictures by greenTEG AG and Flickr
Video Calorimetry: http://www.youtube.com/watch?v=UWksEiJAaLk

Revision History

Date	Revision	Changes
10. October 2013	1.06 (preliminary)	Initial revision
12. February 2014	2.02	Naming revision, updated applications