Looking for Small Changes in Heat Capacity Using A Differential Scanning Calorimeter

By

Will Linthicum

****

Submitted in partial fulfillment

of the requirements for

Honors in the Department of Physics

UNION COLLEGE

March, 2014

Abstract

LINTHICUM, WILL: Looking for Small Changes in Heat Capacity Using A Differential Scanning Calorimeter, Department of Physics, March 2014

ADVISOR: Samuel Amanuel

One of the major difficulties in development of renewable energy is the lack of an adequate and economical means of energy storage. In the case of concentrated solar power a large mass of thermal fluid is required to store a reasonable amount of energy. This is primarily because the fluids tend to have a low specific heat capacity. Formulating composites of these fluids can enhance their specific heat capacity and avails opportunities to make concentrated solar power more attractive. In most cases, the specific heat capacity of composite materials is a weighted average of the individual component heat capacities. This, however, does not take into account interfacial effects where the heat capacity could be different. Although these changes in heat capacity may be small in traditional composites, they could be significant in the case of nano-composites, due to the larger surface area to volume ratios on the nano-scale level. From our phase transition studies of fluids confined in nano-pores, we have demonstrated that the molecules at the interface have different thermodynamic behavior than the bulk material. To study small changes in heat capacity values, we performed systematic studies on empty sample pans and developed a baseline useful in measuring small changes in heat capacity using a power compensated differential scanning calorimeter. Through our measurements we found that leaving the DSC refrigerator running for over twenty-four hours, and proper delicacy in placing the sample pans into the DSC improve the precision of heat flow values.

<u>Introduction</u>

The world is quickly exhausting the limited fossil fuel supply in the earth's crust. Once the fossil fuels are depleted, the human population will face an energy crisis, unless renewable energy sources are developed and improved to become economically practical. Solar energy is an abundant and economic alternative, as 3×10^{24} joules reach the surface of the earth each year, about 10,000 times more than the total global energy consumption [1]. However, solar energy costs $0.22 per kWh unsubsidized to produce as of 2010, which is about five times the cost of coal energy production [2]. For renewable energy sources to be practical, a proper method to store the excess energy is of vital importance. If we can improve the storage of solar energy, we can lower the cost of solar energy production and be a step closer to avoiding an energy crisis and a step closer to a cleaner planet.

A possible method to increase the efficiency of solar energy lies in improving the efficiency of solar energy storage. For solar energy storage, heat transfer fluids such as ethylene glycol or molten salt are used to store excess solar energy gained during daytime to be utilized during peak and night hours. These techniques have round trip efficiencies up to 93 percent [3]. The excess energy is stored as sensible heat, by heating up the fluid, which heats up a tank of water to produce stream which in turn spins a turbine to produce energy, as shown in Figure 1. This results in a heat loss in the heat transfer fluid, which is pumped back to be heated again when excess solar energy arrives, and the cycle repeats. Fluids are used because solids are immobile and gases require a large volume of storage or would require excessive amounts of pressure. If the specific heat capacity of the heat transfer fluid is increased, it will result in more heat being stored per gram of the fluid.
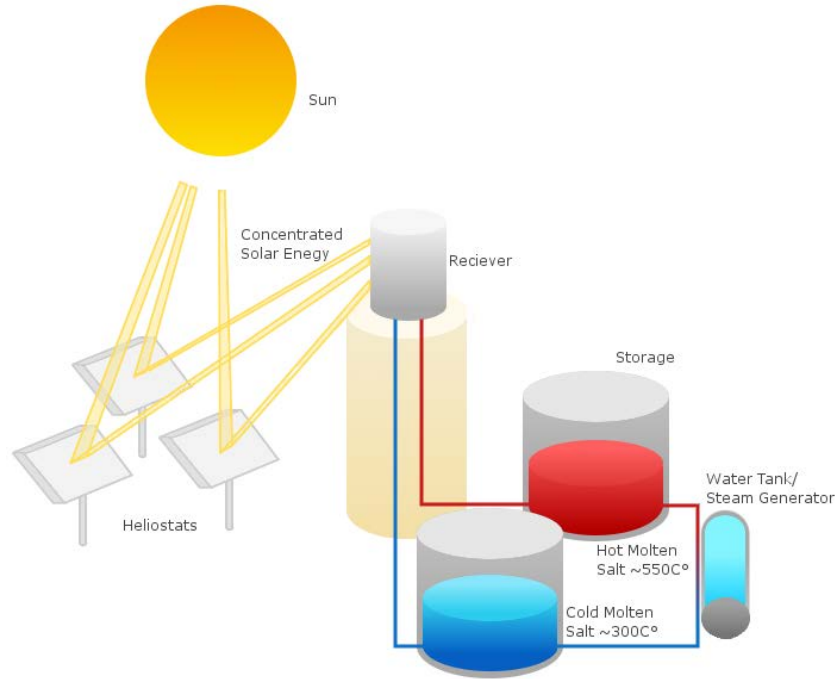
Figure 1. Schematic of the cycle used to store excess solar energy by heating up molten salt to later heat up a water tank when energy is needed.

To improve the specific heat capacity of heat transfer fluids, we tested the effect injecting a heat transfer fluid into silica nano-pores has on the specific heat of the combined system. The current specific heat equation for two substances interacting is:

$$Cp_{composite} = Cp_{particle}\phi_{particle} + Cp_{matrix}\phi_{matrix} \qquad (1)$$

where $Cp_{composite}$ is the specific heat of the composite, $Cp_{particle}$ is the specific heat of the nano-particle, $\Phi_{particle}$ is the weight fraction of the nano-particle, Cp_{matrix} is the specific heat of the matrix, Φ_{matrix} is the weight fraction of the matrix. Equation 1 does not account for a possible change in specific heat at the interfacial, where there are different properties than bulk.

Past experimental observations show conflicting results, both an increase and no change in the specific heat capacities of heat capacity of fluids with addition of nano-particles. An experiment performed by Donghyun Shin and Debjyoti Banerjee at Texas A&M University calculated that the specific heat of a eutectic of lithium carbonate and potassium carbonate increases by ~25% when a silica doped nano-fluid was added [4]. However, Anne K. Starace et al. tested thirteen different combinations of nano-particles and base fluid and saw no increase in heat capacity, and actually noticed a decrease [5]. The contradiction in the results of these experiments motivates our experiment.

For nano-pores, where there is a very large surface area to volume ratio, this interfacial term may be significant. In our studies we observed the effects of the interface on the specific heat capacity of ethylene glycol. We also aimed to observe whether there was a change in the melting/freezing point of the heat transfer fluid when it is confined in nano-pores, as changing the range that the fluid is in a liquid state could allow liquids with high specific heat capacities but high melting points or low boiling points to act as heat transfer fluids.

We predict that there will be a difference in the specific heat capacity of the ethylene glycol and silica nano-pore combination compared to the expected value based on equation 1. If this is true, this knowledge may be applied to increase the specific heat capacities of current heat transfer fluids and ultimately improve the efficiency of solar energy storage. However, we expect the changes in specific heat values to be fairly low, and the precision of our measurements must be very high. Previous work using the Differential Scanning Calorimeter (DSC), used for measuring specific heat capacity, has shown the results are not this precise, as the ASTM standard is not stringent.

To measure heat flow, the DSC heats up two pans, an empty pan used as a reference, and another pan with the sample in it. The DSC heats both up simultaneously according to how it is programmed, and constantly corrects the amount of heat required to keep both pans at the same temperature. The amount of heat used is the heat flow, and is plotted against the temperature of the sample.

To study out hypothesis regarding specific heat changes for nano-composites, we must first improve the precision of the DSC, by observing and troubleshooting random errors that lead to the poor precision. Possible errors include the effects of leaving the refrigerator on for different amounts of time, not allowing enough time for the DSC to stabilize after closing, leaving the DSC sample compartment open too long, and errors induced when physically placing or removing the sample pan.

Experimental

For our experiment, we used empty PerkinElmer LLC 0219-0062 volatile pans to be tested for specific heat capacity using a PerkinElmer Diamond Differential Scanning Microscope. To test, we followed ASTM E1269-11 standards. The DSC tests consist of programming the system to raise the temperature of the sample at a specific rate. The instrument will adjust accordingly, and the heat flow required to raise the sample at the chosen rate is displayed as a function of temperature. Our tests consisted of heating the samples at a rate of $20C^o$/minute over a temperature range of $30C^o$ to $110C^o$.

The purpose of the cooling refrigerator is to keep the heat sink (surrounding) at lower temperature (-80C^o according to the manufacturer) than room temperature. This allows for controlled heating and cooling of the sample for temperatures above -50C^o, as the upper ends of the temperature is limited by the alloying and melting temperatures of the sample holders.To test the effects of leaving the refrigerator on for different periods of time, we performed tests measuring heat flow on an empty sample pan that was left in the DSC after performing tests the previous day, and performed a run every fifty minutes.

As mentioned before, the heat sink keeps the sample at -80C^o. However, when the DSC is opened to load a sample, the sample compartment heats due to the thermal contact with the ambient. This takes the instrument out of its stability and it needs to equilibrate back again after the DSC is closed and the sample is isolated from the ambient. To test the effect of stabilization time on the heat flow values, we left the sample compartment open for one minute, and then waited different periods of time after closing the sample compartment of the DSC before performing our tests. To examine the effects of leaving the sample compartment open for different periods of time, we left the sample compartment open for different periods of time, and then performed runs one minute after closing the sample compartment.

The construction of the DSC is based on the heating elements and thermometers being in intimate contact with the sample. In the case of our DSC, these are placed just below the sample compartment. Thus any slight mechanical stress on the sample compartment can change the baseline of the instrument and thereby subsequent measurements. To observe the repercussions of placing and removing sample pans from the DSC, we would remove and then add the pan back into the DSC between each test, and record the amount of time and the 'difficulty' (whether or not it took a few attempts) in placing the pan back into the DSC.

Results

      To test the precision of the DSC, we performed a DSC run programmed to heat an empty sample pan from $36.85C^o$ to $106.85C^o$, then rapidly cooled the empty pan back to $36.85C^o$, and repeated this cycle a total of five times. We also performed two separate individual runs over this temperature range, using the same sample pan and removing it from the DSC between these tests. The results are shown in figure 2.

      When the pan is allowed to heat and cool multiple times in the same run, the values are extremely precise, as all of the heat flow values agree within 0.1mW over all temperatures. The heat flow values have low precision when comparing the two separate individual runs with the cycled run, as the first run differs by at least 0.5mW over all temperatures with the second run, and by at least 0.8mW over all temperatures for all five repeated tests for the third run.
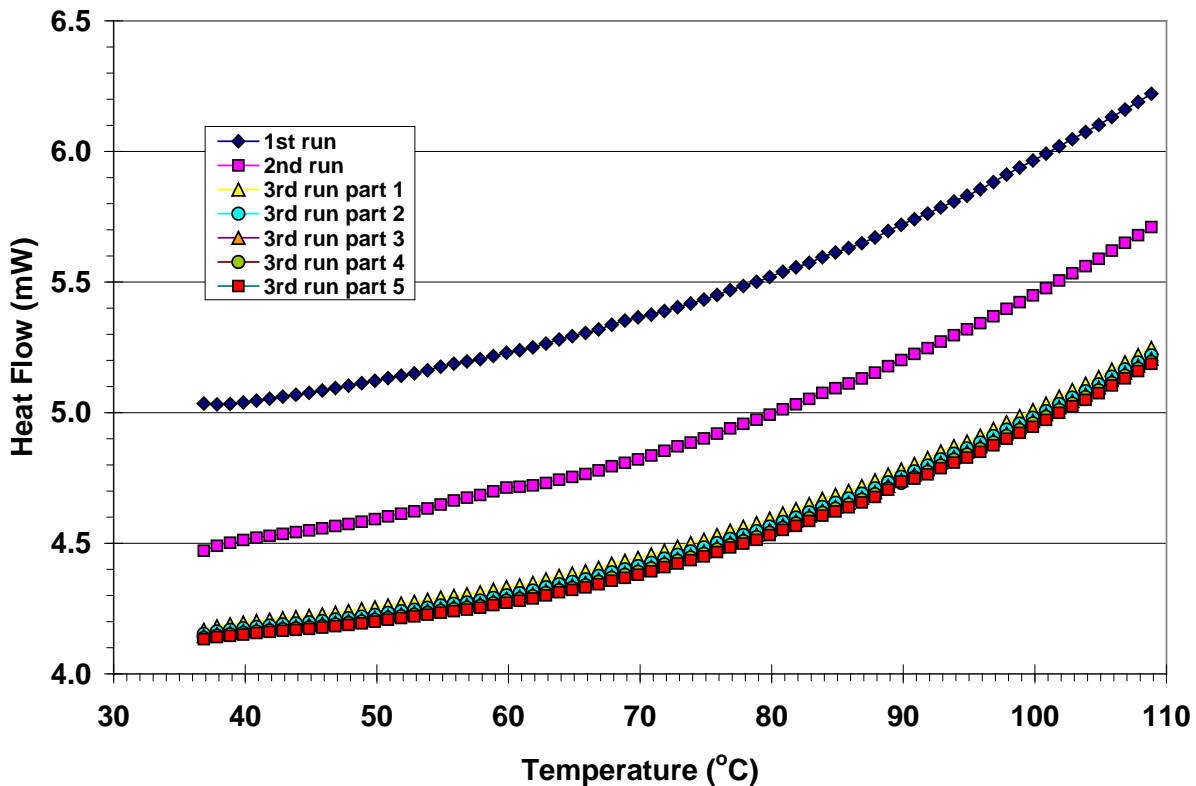
Figure 2. The heat flow values at different temperatures for three runs using the same empty sample pan, two individual runs and one run that repeatedly heated and cooled the pan over the temperature range five times.

To testing if leaving the DSC on for a longer amount of time had an effect on the heat flow values of our measurements, we performed six DSC runs over the temperature range $36.85C^o$ to $106.85C^o$, the first run we performed fifty minutes after turning on the refrigerator of the DSC, and each additional run was taken an additional fifty minutes after the previous run had begun. These results are shown in figure 3.

We notice that the tests we performed had increasing precision as we allowed the DSC to stay on for longer. The first few tests had a difference in heat flow values of at least 0.5mW over all temperatures, while the difference in heat flow values between the second and third run was

less than 0.2mW over all temperatures, and the differences in heat flow values between the remaining adjacent runs were under 0.1mW over all temperatures.
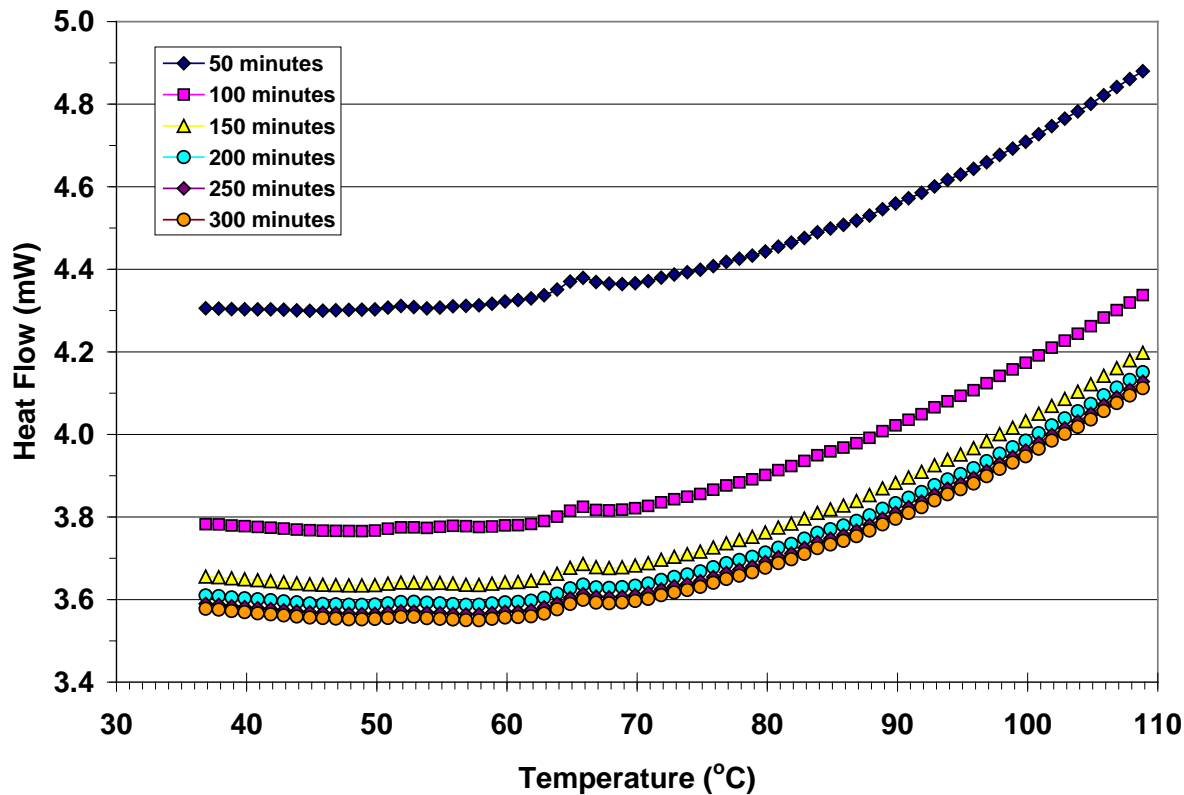

Figure 3. The heat flow values at different temperatures for six runs, taken in fifty minute increments after turning on the refrigerator of the DSC.

To test if there is a relationship between the amount of time the DSC is allowed to stabilize after opening the sample compartment, we performed six tests on an empty reference pan, in which we opened the sample compartment of the DSC for ten seconds for each test, then waited different amounts of time after closing the sample compartment before running identical DSC runs over the same temperature range. These results are shown in figure 4.

Figure 4 shows a downward trend in heat flow values over the chronological order of the tests, which is also present in figures 2 and 3. We have deduced that this is due to the DSC refrigerator running longer. Therefore, we believe there is little effect on the heat flow values when allowing the DSC to stabilize for different amounts of time. However, the DSC run in which we only allowed the instrument to stabilize for thirty seconds does not follow the expected downward chronological trend.
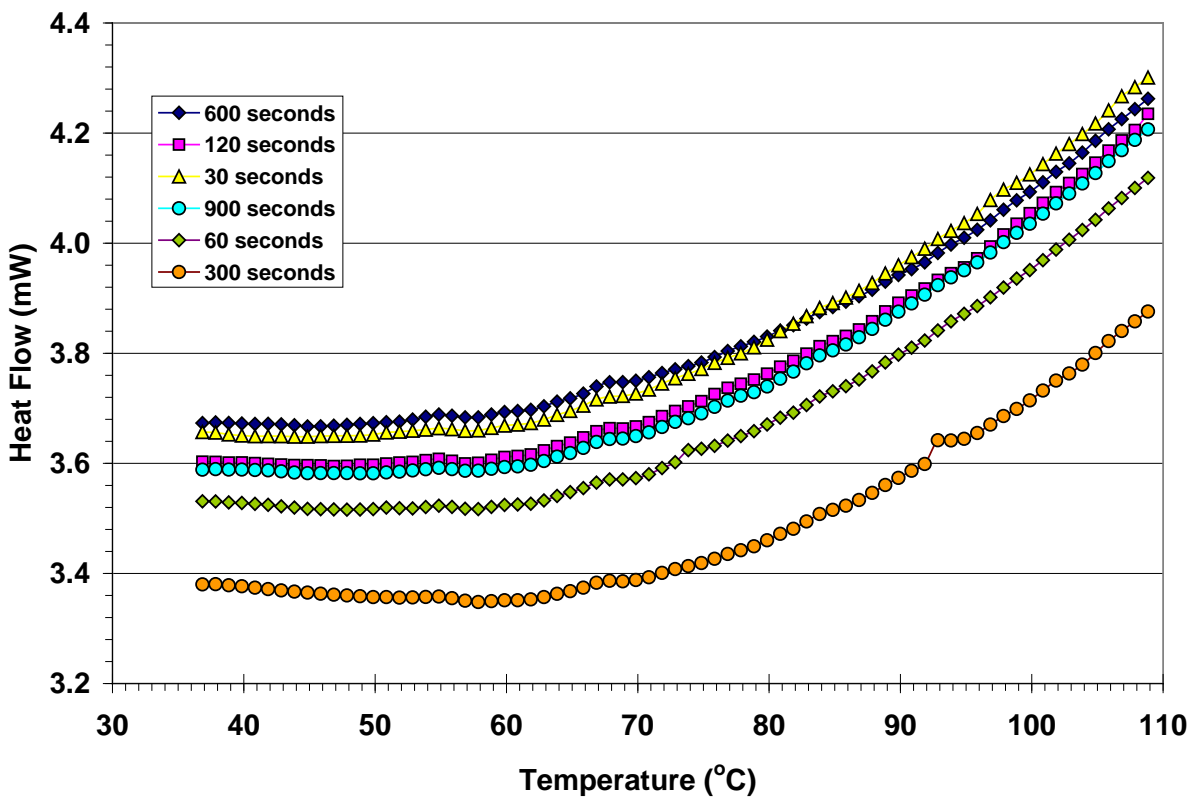

Figure 4. The heat flow values at different temperatures for six runs, each allowing the DSC to stabilize for different amounts of time in randomized order after closing the sample compartment. The DSC was turned on three hours before performing these tests. The table shows the order in which the tests were performed.

We then aimed to see if leaving the DSC on for even longer, over twenty-four hours, improved the precision further. We compared this by performing the same test shown in Figure 4, using the same empty sample pan and without removing it, twenty-four hours later, over the same temperature range. These results are shown in figure 5.

We see an improved precision in results in figure 5 compared to figure 4, as the data ranges over a span of 0.2mW at the lowest temperature of figure 5 compared to a span of 0.3mW at the lowest temperature of figure 4. We also notice there is no downward trend in these results that were characteristic in the first three figures.
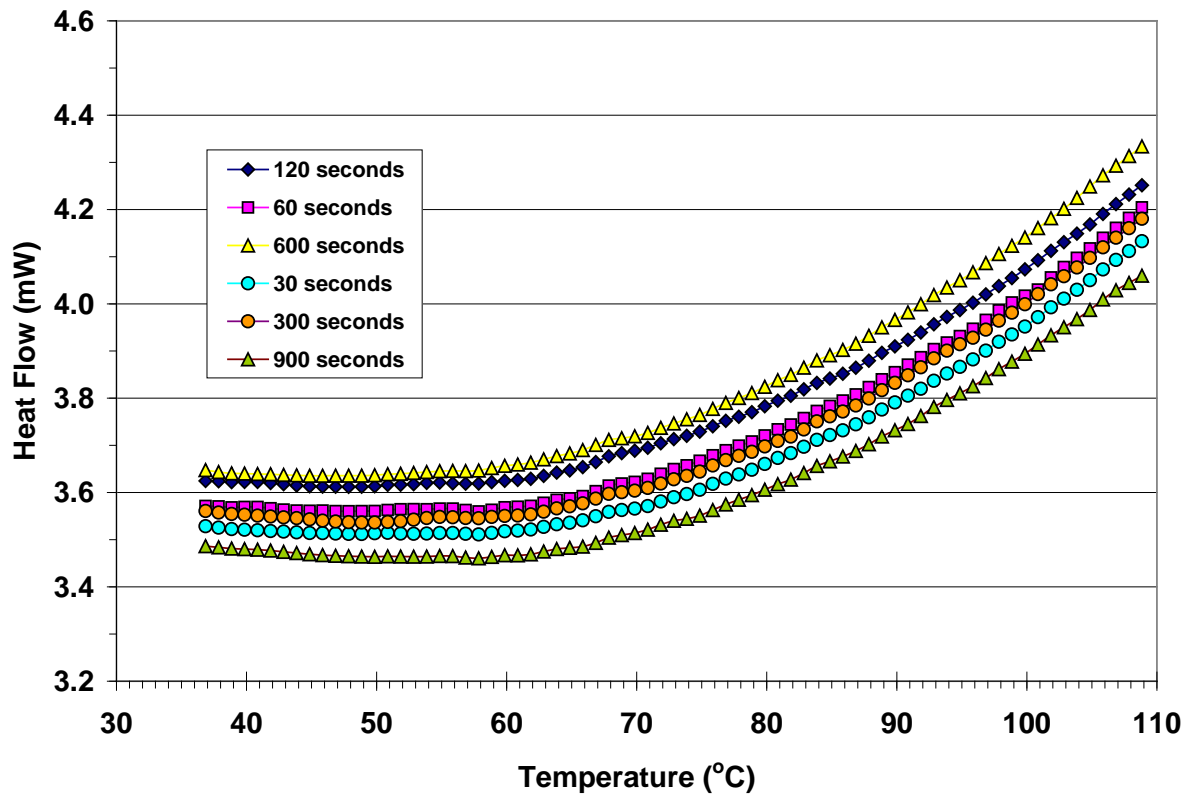
Figure 5. The heat flow values at different temperatures for six runs, each allowing the DSC to stabilize for different amounts of time in randomized order after closing the sample compartment. The DSC was on for twenty-seven hours before performing these tests. The table shows the order in which the tests were performed.

We then tested if leaving the DSC sample compartment open for different amounts of time had an effect on the heat flow values. We would leave the sample compartment open for different amounts of time, ranging from 10 to 320 seconds, and then allowed the instrument to stabilize for one minute, and then performed the run. These results are shown in Figure 6.

We notice a downward trend as seen in figures 1-3, with the exception of the 320 and 260 second terms. The 320 second term is significantly higher than all of the terms, and differs by over 0.2mW over all temperatures when compared to the 40 second test, the test chronologically before it. The 260 run only differs from the 20 second run, the test chronologically before it, by ~0.05mW over all temperatures however. Besides the 320 second run, all tests have heat flow values that agree within ~0.2mW.
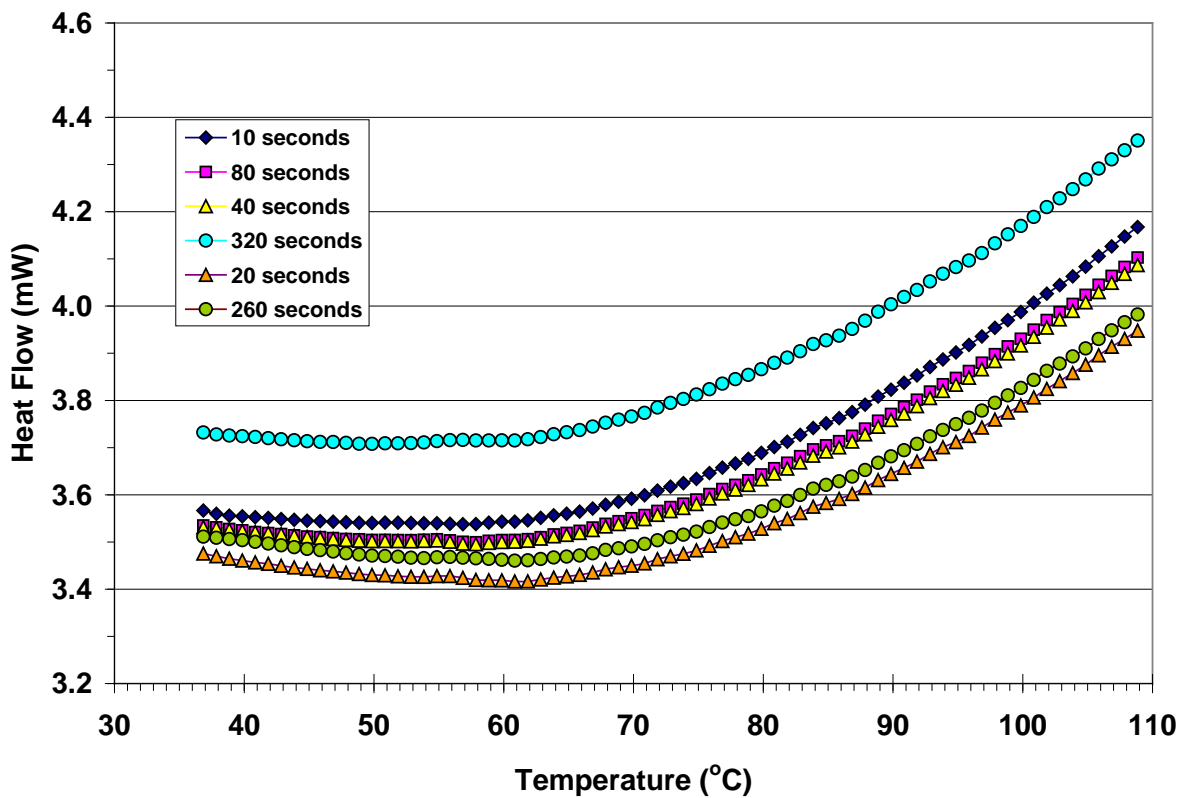

Figure 6. The heat flow values at different temperatures for six runs, each allowing the DSC sample compartment to stay open for different amounts of time, in randomized order. Each run allowed the DSC to stabilize for one minute, and all runs were taken twenty-four hours after turning on the refrigerator of the DSC. The table shows the order in which the tests were performed.

Finally, we tested the effects that removing the pan from the DSC has on the instrument. We performed five runs, removing the empty pan after each run, and replacing the same empty pan back into the instrument. We recorded the amount of time it took to place the pan into the instrument, and whether the process was relatively easy (smooth) or it took some effort that might have caused the pan to harshly interact with the instrument (rough). These results are shown in Figure 7.

We notice that the first two runs agree in heat flow value to a precision of 0.2mW over all temperatures, but there is a large increase in heat flow values between the second and third runs, a rough run, ranging from a 0.9mW to a 2.0mW increase over different temperatures. From there, we see another, but smaller, increase in heat flow values between the third and fourth runs, with differences of 0.15mW to 0.3mW over different temperatures. Finally, we see a decrease in heat flow values between the fourth and fifth runs, with heat flow values agreeing within 0.1mW over all temperatures.
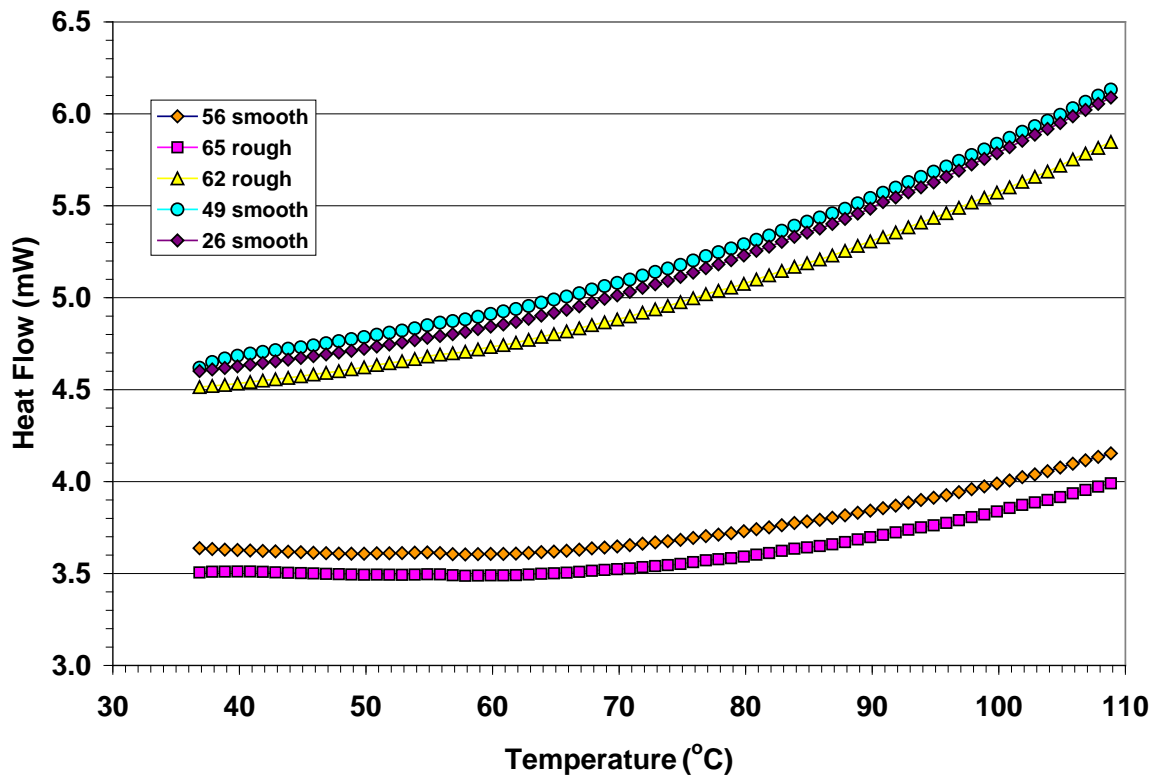
Figure 7. The heat flow values at different temperatures for five runs, between each run removing the empty pan and replacing the same empty pan back into the instrument. Each run allowed the DSC to stabilize for one minute, and all runs were taken twenty-four hours after turning on the refrigerator of the DSC. The table shows the order in which the tests were performed, and describes the amount of time and the difficulty it took to place the pan into the DSC.

Discussion and Conclusions

Upon observing Figure 2, we deduced that the DSC is capable of yielding precise results, as the five parts of the third run all agreed in heat flow values within 0.1mW over all temperatures. However, qualities of our procedure or of the instrument may cause the heat flow values to differ significantly, as the first run in Figure 2 differs in heat flow values by 0.5mW and 0.8mW to the second and third runs respectively. This particular test inspired the remaining experiments, to deduce the cause of the differing heat flow values.

1. Effect of stabilizing the refrigerator: We tested the effect leaving the refrigerator of the DSC on for different amounts of time had on the heat flow measurements, shown in Figure 3, and noticed the results had greater precision as the refrigerator had been left on for longer to reach its thermal equilibrium and stabilize. This test suggests leaving the refrigerator on for longer significantly improves the precision of the results, as the difference in leaving it on for 100 minutes and 300 minutes improves the precision from 0.5mW to 0.1mW when each test is compared to their respective previous runs. This test alone therefore accounts for a large part of the poor precision shown in Figure 2, and lead us to perform our remaining tests only after leaving the DSC on for at least three hours.

We then tested the effect leaving the refrigerator on overnight had on improving the precision of the DSC further. We accomplished this by performing the same experiment performed in Figure 4, but after leaving the refrigerator running for twenty-four hours (shown in Figure 5). We noticed that the results had improved in precision, the highest and lowest heat flow

values differed by 0.2mW in Figure 5 compared to 0.3mW in Figure 4, and the results did not follow the same downward trend we had been seeing. This indicates the results are no longer dependent on the time they are performed, which is the desired result. From this we determined we must leave the DSC on for at least twenty-four hours to obtain results that are independent of how long the refrigerator has been on.

2. How long the DSC need to stabilize after loading the sample: Testing the effect of allowing the DSC to stabilize for different amounts of time, shown in Figure 4, showed trends that match previous trends, such that tests performed later have lower heat flow values, indicated by the refrigerator being on for longer. However, the one exception to the downward trend is the run we allowed the DSC to stabilize for only thirty seconds. To conclude if this is due to the lower stabilization time, repeated experiments must be made. Although this only appears to be a minor difference and not entirely conclusive yet, we have decided to allow all future tests to stabilize for at least a minute before performing the experiment.

3. Inevitable heating of the sample compartment during sample loading: We tested the effect leaving the sample compartment of the DSC open for different amounts of time had on the heat flow values (shown in Figure 6). We noticed a return of the downward trend for the lower values, indicating tests may still be time dependent. Apart from that, we noticed a significant unexpected increase in heat flow values when the DSC was left open for 320 seconds, and a slight abnormality in the downward trend when the DSC was left open for 260 seconds. In order to conclude these times truly affect the heat flow values, additional testing is required. This would

suggest the DSC should be left open for no longer than 80 seconds, which is reasonable, as it typically takes about a minute to successfully place a sample into the DSC. This suggests that the amount of time the DSC is left open for a typical run does not significantly affect the heat flow values.

4. Inadvertently changing the thermal contact of the instrument: We then tested the effect removing and replacing the pan had on the DSC had on the instrument (shown in Figure 7). The large increase in heat flow values between the second and third run, ranging from a 0.9mW to 2.0mW difference depending on the temperature, suggests that the act of removing or replacing a sample pan into the DSC has a significant effect on the heat flow values. We also observe that the heat flow values remain in a similar range after the third run, suggesting the instrument has been permanently altered by the event that occurred between the second and third run.

We have ultimately determined that the most significant changes in heat flow values stem from the amount of time the refrigerator is left open and the physical removal or replacement of the sample pans into the instrument. The refrigerator issue is easily solved by simply leaving the refrigerator on for longer before performing experiments. To solve the issue in removing or replacing pans into the DSC without significantly altering the instrument, we must design a way to systematically perform these tasks. We intend to develop a custom pair of tweezers, utilizing proper alignment and calibration, that will place or grab a sample pan without the risk of moving or damaging the sample holder. If we are able to create this device, we will have reduced most of the issues in precision we have been facing, and we will be able to observe small changes in specific heat capacity values of nano-composites that we aim to study.

Work Cited

[1] Grätze, Michael. "Photoelectrochemical cells". Nature. Vol 414. 2001. Nov 15, 2001

[2] Morgan, Jason. "Comparing Energy Costs of Nuclear, Coal, Gas, Wind, and Solar". Nuclear
Fissionary. Apr 2, 2010. http://nuclearfissionary.com/2010/04/02/comparingenergycosts-
of-nuclear-coal-gas-wind-and-solar/

[3] Biello, David. "How to Use Solar Energy at Night". Scientific American. Feb 18, 2009.

[4] Shin, Donghyun and Banerjee, Debjyoti. "Enhanced Specific Heat of Silica Nanofluid".
Journal of Heat Transfer. Texas A&M University. Feb 2011.

[5] Starace, Anne K. et al. "Nanofluid heat capacities". Journal of Applied Physics. Dec 2011.