Ice Oddities

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Abstract

Apparatus to Measure Specific Heat. Sara E. Yancey (Virginia Tech (VPISU), Blacksburg, VA 24060) Elizabeth Fenstermacher (Mount Holyoke College, South Hadley, MA 01075), Jerry Seidler (University of Washington, Seattle, WA 98195).

The goal of my summer was to start a new experiment under the direction of Jerry Seidler. Eliz Fenstermacher and I researched, designed, and built an Peltier AC Calorimeter (PAC) for the measurement of the specific heat of water in a water/oil emulsion. The goal of the experiment is to control the temperature of the emulsion and determine the specific heat as a time and temperature dependent quantity. The summer ended with all equipment completed, but no data taken.

1 Introduction

Water is a solvent, medium, or participant for almost all environmental reactions. There is almost 10 billion km^3 of it on the earth; water controls our bodily functions and weather. Certain characteristics are well known, and often used as the standard with which to base units (for example, the calorie is the energy require to raise 1g of water 1 degree C). However, water does not always live up to these standards we impose on it. Water behaves much differently than one would calculate from its enclosed atoms. The viscosity, surface tension, and heat capacity are all much higher than would be for many similarly-massed molecules. The hydrogen bond between neighboring water molecules is known to give these unusual traits.

The goal of this research is to find a way to store biological materials (such as blood and viruses) safely and affordably. If you freeze blood for storage and shipment, the crystalline structure of ice will tear apart the living cells. One option would be to force the liquid into a glassy state (around 170K), thus retaining original composition. To find a plausible solution, we first must learn more about nucleation and surface premelting.

When you cool a liquid, it is possible to cool it well below the melting point and keep it in a liquid state. This supercooled liquid is said to be in a metastable state. When water does change to crystalline ice, it does so very quickly with a process called nucleation. Nucleation is the rapid changing of a metastable state to a stable state with little initial provocation. You may have experienced this in your own home.

This experiment deals specifically with studying the anomaly of premelting. Upon heating, the surface of a bulk solid *premelts*; a layer forms on the surface which is a metastable state of liquid and solid water. This occurs because molecules on the surface are less tightly bound and therefore can acquire more energy – enough energy to change phase. To observe this effect, we look at the specific heat of water droplets in decane, a water/oil emulsion. An emulsion is used in order to maximize the surface area-to-volume ratio, an important factor when looking for surface deviations.

This summer, Eliz Fenstermacher and Sara Yancey designed and built the apparatus needed for Jerry Seidler's group to perform measurements of heat capacity. This will be used in thermodynamic studies of surface premelting.

2 Background

2.1 PAC calorimetry

AC calorimetry, also known as *temperature-modulated calorimetry* is a form of calorimetry that uses a fluctuating heat source. Typically, this means a heat source is applied and T_{sample} is raised. When applied power ceases, heat flows from the sample to the bath. This results in the bath continually growing hotter and the heat source expending more energy than needed.

For our experiment, we used a design for Peltier AC Calorimetry(PAC) [4]. PAC maximizes the peltier effect by using thermocouple wires as the heat source, heat sink, and thermometer. When current is driven one direction, the thermocouple is a heat source, driven the other it is a heat sink. A sine wave T_{sample}, with amplitude Q_0, frequency ω and average temperature T_0 is created.

$$T_{sample} = Q_0 sin(\omega * t) + T_0 \quad (1)$$

In traditional methods, there is only heating, thus $T_{sample} > T_{bath}$ and this ΔT creates a DC offset.

Another benefit of PAC is the versatility. The frequency can be fixed such that the heat does not have a chance to diffuse to or from the bath. The frequency can also be tuned to observe time or frequency dependence.

When dealing with small samples, the massive heater and thermometer used to probe (also called adenda) could display more effects than the sample itself. PAC uses thermocouples made with fine wires of negligible mass.

2.2 Thermocouples

A thermocouple is two distinct wires acting as a heat source or heat sink, depending on the direction current is applied. The type of junction between wires does not matter, as long as it is electrically conductive. In our case, we use one thermocouple pair as a AC heater and another as a thermometer. The theory behind thermocouples is easy to understand, but requires much work for the math behind it. The Seebeck effect occurs when one applies heat to one end of a conductor, thus energizes the local electrons. These "hot" electrons then diffuse to the cold side, resulting in a negative charge on the cold side of the conductor and a potential difference. This voltage is proportional to the difference in temperature between the two ends.

When two dissimilar metals are electrically joined, they exhibit the Peltier effect. This effect deals with the chemical potential of each metal and the work needed to move electrons across the junction. The result is a connection that can act as a heater or thermometer. If current is driven in one direction, the thermocouple is a heat source. If driven the opposite direction, it acts as a heat sink. If current is not driven, and voltage is read, the thermocouple acts as a thermometer.

The major benefit to using thermocouples is the negligible mass they contribute. When working with milligram scale samples, adenda would typically be magnitudes larger than the sample. Data would be that of the adenda and not of the sample.

In our case, we want to measure the specific heat of 10mm^3 volumes of emulsion. We used 12 μm wires [0.0005in] Constantan and Chromel wire acquired from California Fine Wire. To weld a junction between such small wires, we had to build a spot welder, based on that of Garfield [1].

3 Experiment

3.1 Spot Welder

Using the design and circuit made by Garfield [1] we created a spot welder for 12μm thermocouple wires. The design involves a copper block with clips for wires on an x-y translation stage. A spring-loaded copper tip is lowered from a z-translation to the point where the wires cross. The circuit is connected to the tip and ground to the block. When enough resistance is measured across the tip-block connection, a button is manually depressed and the circuit sends a shock across the tip. The amount of shock distributed can be controlled by a dial.

For the circuit, Bryan Venema ordered the required parts and created a circuit board for the specific application. Everything was connected and mounted in an aluminum box with exterior wall plug, dial, button, and feedthroughs to tip and block.

Some of the numbers in the circuit did not work out as expected, so an older version [2] of the same idea was found for clarification.

After welding each thermocouple, we then glue it to a nylon washer with GE 7031 varnish. This washer is for stability and will not effect the electric conductivity of the wires. Each washer-thermocouple set will be used as a heater or thermometer.

3.2 Aluminum Cells

In order to satisfy time constants, we must work in rough vacuum, thus we must contain our drop of emulsion. To do so we used cells from a Differential Scanning Calorimeter made by Shimadzu. The press was found in a chem lab by Lane Seeley. The cells are formed by placing a small Al cup on a die, filling the cup, then placing a thin Al disk on top. The cell is then pressed together by two dies, controlled by rotating a handle. These cells are supposed to hold vacuum for water and we found this to be true. In the case that a stronger seal is needed (if the water should need to boil), additional dies are available through Shimadzu.

Hopefully, the effects of the cells can be subtracted out by testing cells empty, filled with water and filled with decane. The mass of the cell is roughly 25mg and the water it contains roughly 20mg.

3.3 Emulsion Generator

Previously, emulsion generators seem to be expensive blenders with inconsistent emulsion size and quality. However, to create our emulsion we followed the design of Umbanhowar [3]. This technique involves spinning a continuous oil phase such that it maintains a constant velocity. A capillary tube is inserted, and a water/surfactant mixture is pushed through the tube and into the oil. The drops from the capillary are held together with surface tension and are broken off by the drag of the oil. This quickly produces uniformly-sized droplets. For micelles 20μm in diameter, the deviation is 3%. Variables include tip size, continuous phase velocity and (water) jet velocity. The emulsion will be observed under a video microscope to check for deviation.

For our continuous phase, we use decane. In previous papers, hexadecane was used, but it tended to freeze when spun. The melting point of decane is -30^{o}C, and the emulsion generation will take place at room temperature. For our surfactant, we used Span 65. This was consistently used throughout the literature. Both chemicals were purchased through Sigma Aldrich. The motor used to propel the teflon cup was ordered from MicroMotors. The mounts and teflon cups were made by Eliz and Sara.

3.4 Calorimeter

The calorimeter is built by creating the emulsion, filling a cell and sealing it, and then placing one thermocouple on each side of the cell. One thermocouple acts as a heater and another as a thermometer. The washer-thermocouple-cell-emulsion assembly is then placed inside a brass vacuum can. This can measures 4" tall and 2.5" in diameter and is sealed by an indium ring. A 0.5" diameter 0.005" thick stainless steel pipe is then welded to the top of the can. The assembly is then placed in a 4" inner diameter glass dewar made by Bob Morley. A 10" diameter top plate holds a cajon fitting for the pipe, a release valve for N_2 gas and a feedthrough for copper wire in the case a heater is added to the exterior of the cryostat can. The top plate can be screwed onto the flange for the dewar, or mounted onto a N_2 storage container found in the lab. The pipe then connects to an aluminum box that holds copper and thermocouple feedthroughs, release valve, and vacuum pump attachment. The Al box, stainless steel pipe and cryostat will be kept at rough vacuum. The dewar will be chilled with liquid nitrogen until all water droplets have frozen. The temperature is then increased until the desired temperature is reached. Equation 1 is then used to find the specific heat C_p, where T_{AC} is the amplitude of temperature response, ω is the driven frequency and Q is the heat given to the system.

$$C_p = Q/(\omega * T_{AC}) \qquad (2)$$

4 Conclusions

We have completed the construction of the Peltier AC Calorimeter, but have taken no data. Jerry Seidler and graduate student Adrianne Battle will continue on with the project.

5 Literature Cited

References

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