Appendix A. 2-Drop Calorimeter Student Handout

CHEMISTRY 356-358, Physical Chemistry Laboratory

<u>The Cutting Edge of Experimental Thermodynamics:</u> <u>Isothermal Heat Conduction Calorimetry</u>

A physical chemistry laboratory experiment under development at Drexel University, with the cooperation of scientists and engineers at Dow Chemical Company and Lund University, Lund, Sweden.

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Objective: To explore the use of isothermal heat conduction calorimetry as a means of measuring a variety of heat changes such as determining the enthalpies of vaporization and reaction, evaluating the radiant power of a light source, measuring the heat of water adsorption of zeolites and identifying the heat of metabolism from small insects.

Introduction: Calorimetry is the measurement of heat. All chemical reactions and processes and all biological processes, which are ultimately chemically based, are accompanied by the generation or absorption of heat. Thermodynamics, the science underlying the interpretation of calorimetric measurements, is extremely well understood and allows for the determination of many useful chemical properties of substances.

Types of Calorimetry

Because of the central importance of energy changes in chemical reactions, calorimetry is usually a part of any experimental chemistry curriculum. Most general chemistry texts and physical chemistry lab manuals mention one type of calorimeter, the *bomb*

calorimeter. By measuring the heat change in reactions in which the standard enthalpies of formation are known for all but one of the reactants or products, the unknown enthalpy of formation can be determined. Bomb calorimeters are used for determining enthalpies of combustion of organic compounds but are limited in the type of heat changes that could be measured.

Calorimetry as practiced in both academic and industrial research labs, however, is much more diverse. In current literature, forty-four researchers in thermodynamics identifying important areas for development in the 21st century hardly mention combustion calorimetry, but describe dozens of applications of heat conduction calorimeters(Letcher, 1999). Common types of calorimetry are:

<u>Solution calorimetry</u>: a method of measuring the total heat evolved in a chemical process in solution, the process being carried out inside an adiabatic container such as a dewar flask.

With the proper kind of solution calorimeter, one can measure the heat evolved or consumed in fast reactions carried out when one reactant is incrementally added to another. Such experiments are called *thermal titrations*, and they have been widely used in biochemical systems to determine both enthalpy change and binding constant for the formation of enzyme-substrate complexes.

Differential scanning calorimetry (DSC): a method of comparing the heat capacities and heat generation or absorption within a sample and a reference as the temperature of both is raised at a constant rate.

<u>Thermal gravimetric analysis (TGA)</u>: the loss of mass of a sample is continuously monitored as the temperature is raised at a constant rate. Although

not strictly a calorimetric measurement, thermal gravimetric analysis is often combined with differential scanning calorimetry; the acronym is *DSC/TGA*.

If the molar enthalpy change for a reaction is already known, measuring the rate of heat evolution in slow reactions determines the time dependence of the extent of the reaction and thus the rate of reaction. With calorimeters of high sensitivity it is possible to measure the heat given off by an unconnected dry cell battery as it slowly loses its chemical energy, an explosive as it slowly decomposes on the shelf, or even the heat generated by an exercising insect or a germinating seed.

Comparison of Adiabatic and Heat Conduction Calorimetry

Both the bomb calorimeter and the solution calorimeter are examples of **adiabatic calorimetry**. When a chemical process occurs in an adiabatically isolated system of known heat capacity, *C*, the temperature change, ΔT , is measured and the heat change is calculated from the equation:

$$Q = C\Delta T$$
 Equation A-1

In heat conduction calorimetry, the reaction vessel is isolated adiabatically from its surrounds except for contact with a heat flow sensor, which in turn is connected to a large heat sink such as a constant temperature bath. The heat flow sensor generates an output voltage proportional to the flow of heat, dQ/dt, through the sensor from the reaction vessel to the heat sink. This heat flow sensor signal is recorded as a function of time, and the total heat generated in the process is obtained by **integrating the heat flow signal over the duration of the experiment:**

$$Q = \int \frac{dQ}{dt} * dt$$
 Equation A -2

Heat Flow Sensors – Thermocouple Plates (TCP)

The key to making heat conduction calorimetry practical is the availability of sensitive and relatively inexpensive heat flow sensors. Ingemar Wadsö(Wadsö, 1997) has pioneered the use of thermopiles as heat flow sensors. They are commercially available in the form of thermoelectric heat pump(Melcor, 1995) devices that operate on the inverse Peltier effect. The Peltier effect is responsible for the generation of a thermocouple voltage signal. Two dissimilar conducting materials (such as copper and constantan wire), connected at two points of differing temperature, generate a voltage difference proportional to the temperature difference. In the inverse Peltier effect, a flow of current through two dissimilar conductors causes a temperature difference to develop across the two connection points of the dissimilar materials. In a thermoelectric heat pump, when a voltage is applied to a thin array of dissimilar conducting pairs of materials, heat is pumped from one side of the array to the other side. In the commercial devices, the dissimilar materials are small rectangular pieces of n- and p- doped BiTe semiconductors. Thermoelectric heat pumps are used, for example, in cooling the integrated circuits used in computers. Figure A-1 depicts the structure of the type of thermocouples used (Tellurex, 2002). The two-drop calorimeter was constructed using TCP, CP1.4-71-045L from Melcor (Trenton).



Figure A-1. Thermocouple Plate (TCP) (Tellurex, 2002)

One TCP is comprised of a large number of thermocouples connected in series electrically to give a high output voltage. They are connected in parallel thermally to give a high ratio of output voltage with a temperature difference.

The Working Equations for a Heat Conduction Calorimeter

The Tian equation is employed to calculate the thermal power from the measured signal. The output voltage, U(V), from the heat flow sensors recorded as a function of time may be converted into the heat flow rate, P(W), by multiplication with the calibration coefficient, ε (W/V). If we are interested in the kinetics of rapidly changing processes the Tian equation takes into account the heat capacity and the rate of temperature change of the reaction vessel(Bäckman *et al.*, 1994).

$$dQ/dt = P = \varepsilon (U + \tau^* dU/dt)$$
 Equation A-3

Here τ , the time constant, of the calorimeter is given by

$$\tau = C / k$$
 Equation A-4

Where C (J/K), is the heat capacity of the sample and its holder cup and k (W/K), is the heat conductance of the TCP. The calibration coefficient, ε (W/V), takes into account the thermal conductance of each thermocouple divided by the material constant of the thermocouple(Bäckman et al., 1994). The calibration coefficient is usually found from electrical calibrations, as discussed below. Using **Equation A-3**, when the signal, *U*(t), is numerically differentiated to give, dU/dt, the actual thermal power produced in the sample from the measured voltage may be calculated.

When the thermal power changes slowly, at steady state conditions, dU/dt = 0. The Tian equation maybe reduced to:

$$P = \varepsilon * U$$
 Equation A-5

For the experiments described here, the reduced form of the Tian equation, **Equation A-5**, may be used.

Design and Construction of a Simple Heat Conduction 2-Drop Calorimeter

Thomas C. Hofelich, a chemist in the Analytical Sciences Laboratory at Dow Chemical Company, has developed a sensitive and inexpensive heat conduction calorimeter, which he has used extensively at Dow for measuring heat production when small quantities of reagents are mixed(Hofelich *et al.*, 1994). Hofelich calls his device "The

2-Drop Calorimeter," because the heat evolved when one drop of reactant A is added to one drop of reactant B can be measured.

Dr. Lars Wadsö, an engineer at the Division of Building Materials, Lund University, Sweden, has also developed a similar, inexpensive, isothermal heat conduction calorimeter(Wadsö, 1998). Experimental applications he has developed include:

Polymer science:	Curing reaction of a standard epoxy
Food science:	Microbiological growth in food
Material science:	Steel corrosion
Coatings technology:	Oxidation of linseed oils
Biotechnology:	Heat production in waste compost

Commercial versions of the type of calorimeter described here have recently been introduced. Typical industrial uses include the determination of the heat evolved upon mixing materials of both known and unknown origin (hazardous evaluation), and the study of the effect of concrete additives on the hydration of cement paste (Hofelich *et al.*, 1997; Wadsö, 1998).

In this experiment, a 2-drop calorimeter constructed at Drexel from Hofelich's and Wadsö's plans will be used (Hofelich, 1997). The sample chamber of the 2-drop calorimeter is a small glass vial of 2 cm³ volume. Inside the insulated box housing the calorimeter, the sample vial rests in an aluminum cup in good thermal contact with a Melcor thermopile resting on a large aluminum block functioning as a heat sink. There are two identical thermopile – aluminum cup – sample vial combinations, one serving as the **reference** and one serving as the **sample chamber**. **Figure A-2** is a schematic picture (Wadsö, 1999) of an isothermal heat conduction calorimeter.



Figure A-2. Isothermal Heat Conduction 2-Drop Calorimeter

Calibration of the instrument

Thermal calibration of the 2-drop calorimeter is achieved by applying a known voltage,

V, across a resistor of resistance, R, attached to the side of the aluminum cup where:

$$V = I * R$$
 Equation A-6
 $P = I * V$ Equation A-7

thereby leading to:

 $P = V^2/R$ Equation A-8

The thermal power generated in the resistor is:

$$dQ/dt = P = V^2/R$$
 (W) Equation A-9

When a steady state output voltage is obtained, the calibration coefficient may be found from

$$\varepsilon = P/U$$
 (W/V) Equation A-10

where U, is the total measured voltage output. Typical values of ε , for commercially available thermopiles are 2.4 – 2.5 W/V. Figure A-3 depicts a typical steady state output voltage used during the calibration.



Figure A-3. Calibration thermal signal for 2-Drop Calorimeter

Enthalpy of Vaporization of Organic Solvents

The 2-drop calorimeter provides an easy method for determining the enthalpies of vaporization of volatile organic solvents. As only one drop of the solvent is released into the aluminum cup, the thermopile reads the endothermic event as the solvent evaporates and the thermal signal is gathered. By measuring the mass of 20 drops of

solvent and using the solvent's molecular weight calculating the mass of one drop, we can compute the molar enthalpy of vaporization of the solvent.

The calibration coefficient from the calibration is used to convert the voltage (U) to a thermal signal (W). Integration of the area under each thermal signal curve, U, gives the heat signal, Q, in Joules. Using the measured heats and the amount of solvent in each drop, the molar enthalpy of vaporization is found:

$$\Delta_{vap}H = \frac{\varepsilon \int Udt}{n}$$
 Equation A-11

Here, *n*, is the moles of solvent.

Laser Power Meter

The TCP used in the 2-drop calorimeter are sensitive enough to be used as a laser power meter. In this experiment, the radiant power of a light source, a helium-neon laser, is measured. The 5 mW laser will be directed on the top surface of the sample aluminum cup blackened with graphite. After leaving the laser on for a few minutes, a steady-state output voltage will be reached. The output voltage, U, multiplied by the calibration coefficient, ε , gives the thermal power (W). The percentage of light absorbed and reflected can then be found

$$\{Power_{(measured)} / Power_{(radiated)}\} * 100 = \% absorbed$$
 Equation A-12

Thermal Titration of Tris(hydroxymethyl)aminomethane, (THAM), C(CH₂OH)₃NH₂, with 3M HCl

Using heat conduction calorimeters, thermal titrations carried out when one reactant is incrementally added to another enable the measurement of the heat evolved in fast reactions. This method has been widely used in biochemical systems to determine both the enthalpy change and the binding constant for the formation of enzyme-substrate complexes. Performing a thermal titration in this calorimeter requires only microliters of the titrating solution. In this experiment, a small sample of reagent A, either solution or solid, is placed in the vial, and the titrating reagent B is held in a 1000 μ l syringe mounted above the vial. Single drops of B are added to the vial, and the thermal signal generated from each addition is recorded.

As the first drops of titrant are delivered, a large exothermic signal is seen. Two or three drops at a time are delivered after the signal returns to the baseline. Releasing the drops of titrant is repeated until the expected equivalent molar volume is achieved indicating that the endpoint is reached. The titration proceeds according to:

 $H^{+}(aq) + Cl^{-}(aq) + C(CH_2OH)_3NH_2(aq) \rightarrow C(CH_2OH)_3NH_3^{+}(aq) + Cl^{-}(aq)$

Equation A-13

The volume of HCl required to neutralize all of the THAM is used to determine the enthalpy of reaction for this titration. At any intermediate point in the titration, the ratio of the added volume to the total volume of HCl equals the ratio of the added number of drops to the total number of drops.

The number of moles, n_i , in each drop of titrant is, $n_i_{(HCl)} = V_{i HCl} * M_{HCl}$, where V_i , is the volume of titrant used and M, is the molarity of the titrant. Each peak,

corresponding to the ith drop of the titrant, is integrated to give the heat, Q_i (J), Equation A-2. The total heat in all peaks before the endpoint, $\Sigma_i Q_i$, divided by the moles of titrant added before the endpoint, $\Sigma_i n_i$, gives the enthalpy of the process.

Another method of calculating the enthalpy of reaction is to employ the moles of THAM used. Because of difficultly in seeing the syringe gradients, we will be using Equation A-15, the moles of THAM for our calculations.

Using the literature value(Eatough *et al.*, 1974) for the enthalpies of formation of all reactants and products, Hess's Law is used to calculate the $\Delta_r H$. We assumed no concentration dependence for the $\Delta_f H$ (s).

Insect Metabolism

Isothermal calorimeters have been explored as a means of measuring the heat of metabolism of small insects. The rates of heat exchange between small insects and their environments are believed to be controlled by several factors: radiative heat gain, convective heat loss, metabolism, and evaporation. These properties vary with the size, shape, orientation, and surface properties of the insect(Casey, 1988).

Isothermal microcalorimeters offer a non-damaging route to monitor the metabolism of insects. To simplify the multiple sources of possible heat exchange, the heat measured from an insect scurrying in the vial is taken as the heat of metabolism. The heat

measured is the sum of the heats from all of the insect processes that takes place in the calorimeter.

The integration of the peaks, Equation A-2, corresponding to the activity events, gives the heat, Q, in Joules. If we assumed that the heat evolved from the bug is all the heat of metabolism, it is interesting to try to calculate how much sugar is needed to generate the same amount of heat. An approximate value can be found by using the "burning" of glucose in oxygen as a model of metabolism.

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$
 Equation A-16

From the Δ_f H of the products and reactants, the Δ_r H can be found from Hess's Law. We can use this to determine the amount of glucose that would produce this amount of heat.

mass _{glucose} (g) = (
$$\Sigma_i Q_i * 180 \text{ g/mole}_{glucose}$$
) / $\Delta_r H_m$, _{glucose} Equation A-17

Heat of Water Adsorption on Zeolites

Zeolites, or "molecular sieves" have a porous structure. The internal surface area of these pores is quite large (several hundred square meters per gram of zeolite). Zeolites used as molecular sieves usually come as spherical pellets with diameters of ca. 1-2 mm. When even a few milligrams of dry zeolites are exposed to water vapor, large exothermic heat flows are observed. Carefully keeping the zeolites in a dry environment is essential prior to the experiment or during the prep time. In this lab period, the exothermic event will not reach completion. We will therefore only use a ten-minute period of the water adsorption event to calculate the $\Delta_{absorption}$ H of the

zeolites. The enthalpy of the adsorption process for this time period and mass of zeolites is found:

$$\Delta_{adsorption}H = \frac{\varepsilon \int Udt}{masS_{zeolites}}$$
 Equation A-18

which then yields the ΔH in Joules/gram.

Procedure

Data Acquisition Setup:

- 1. Put the top part of the insulating box on the calorimeter. This will allow the instrument to reach thermal equilibrium while setting up the computer interface and preparing for data acquisition.
- 2. Make the necessary connections from the calorimeter leads to the A/D computer interface terminal board. A single-ended setup is used. One lead is connected to pin 1 and the other to pin 18. The polarity (-/+) is arbitrary. If it is reversed, the magnitude of the signal remains the same, but the sign of the signal will change.
- 3. On the computer, open the **Agilient VEE Pro 6** software. There should be a shortcut on the desktop, if not, the software can be opened through Programs and Agilient VEE.
- 4. Close the "Tip of the Day". Open a new file. In the folder VEE Programs, open **two_drop**. You will see the following control panel open:



Figure A-4. VEE control panel for data acquisiton of 2-Drop Calorimeter experiments.

- 5. On the A/D config icon, double click in the "Configure" box. The **channel** should read **0**, the **gain** is **8**, and the **sample rate** is **1 Hz**. Click on the "Hardware" tab on the right hand side. Make sure the "**channel type**" is "single-ended."
- 6. In the "Get Data Panel," the **channel** should read **0**, and **points** are **1**.
- 7. Right click on a plain light blue part of the "strip chart." A submenu will appear for the "y plot." Select the "properties" option. Go to the "scales" tab. (Do not use the auto scale option because the graph constant updates, it will be difficult to see any changes unless you are following the "AlphaNumeric" display.)
- 8. Change the X Name to "Time (s)" and the Y Name to "Volts". For the X, or Time axis the maximum should be 100 and the minimum should be 0. For the Y, or Volts axis, change the scale to 5m for the maximum (meaning 5 mV) and -5m for the minimum. (N.B. Your *data is still recorded in volts*, this is just scaling or magnifying the axis of the chart so that we will be able to see the signal.) The Y scale may be changed for any of the experiments.
- 9. It is crucial to **save the data** to a file for later data analysis. In the light blue section of the "**To File**" look for the raised light blue box, next to the words "To file:" Double click in there and at the bottom type in a name for your file. It will put the correct file extension, you just need to type in a name for the particular par tof the experiment (e.g. calibration). You may want to further distinguish the file with your initials or the date. This will save the data in the file "VEE Programs." Afterwards, you can move the file to your own folder under "My Documents."
- 10. You can start the data collection in one of two ways click on the green "start" button or click on the ▶ on the toolbar at the top.
- 11. Start the data collection to record the thermal baseline. You want to collect about 5 minutes of a stable baseline before starting the calibration.
- 12. In between each experiment, be sure to change the file name according the experiment being performed.

Calibration of the Calorimeter

- 1. While data for the baseline is being recorded, use a **voltmeter** to **measure the voltage of the battery** that you will use as your potential source.
- 2. Also **measure the resistance** of the resistor attached to the side of the sample aluminum cup and record its value. Al $k\Omega$ chip-resistor is used as the heating element. However the thin copper wire leads on the resistor also impose some resistance. Measuring the resistance using an ohmmeter will account for this

extra resistance. The resistor is used only for the calibration and does not play a part in any of the other experiments.

3. Close the electrical circuit (turn on the switch, if one available) by connecting the battery to the leads from the calorimeter. After a few seconds (depending on the time constant) you will see a decrease (or increase depending on the polarity of the leads in the terminal board) in the signal indicating an exothermic process from the heating of the sample cup. Since the thermopiles are heat flux sensors, the signal will decrease in magnitude and eventually reach a steady state and level off. After a few minutes (e.g. 5 min.) disconnect the battery and the signal will return to the base line. Wait a short while to establish a baseline after the **heating event**. Repeat the calibration **two more times** and then stop logging data by clicking on the stop program (■) on the toolbar.

Experiment 1: Enthalpies of Vaporization

- 1. Weigh a clean glass vial and a lid. Fill a syringe with the organic solvent. Release 20 drops in a glass vial, cover to prevent any evaporation and find the mass. After finding the mass of 20 drops, divide to find the mass of one drop. Use the molecular weight to determine the amount of moles in one drop.
- 2. Fill a 1 ml syringe to the 0.5 ml mark with the organic solvent. Mount the syringe on the sliding top and align the syringe exactly above the aluminum sample cup (the one you calibrated that had the resistor attached to the side). You may lower the syringe a few mm into the cup, but the syringe should not touch the sides or the bottom of the aluminum cup.
- 3. Tighten all screws and put the insulating box on the calorimeter so that the syringe extends through the hole in the top part of the insulating box. Allow for thermal equilibrium to be reached.
- 4. Prepare for data acquisition in the same manner as described in the calibration procedure. Remember to **change "To file" name**. **Start logs** and keep recording the signal for a few minutes(e.g. 5min). This will provide for a **baseline** before the actual event.
- 5. Start pushing down the plunger on the syringe very slowly until you observe a change in the signal. This will indicate that a drop has disengaged from the syringe tip and has fallen into the aluminum cup. It is difficult to see the actual event. An **endothermic signal** will be observed until all of the liquid is vaporized. The signal will eventually return to the baseline.
- 6. Record a **few minutes of baseline before starting the next drop. Repeat** the measurement **twice more** after which time you can "stop" the data acquisition.

Experiment 2: Laser Power Meter

- 1. Use a ring stand to secure the He-Ne laser above one of the aluminum cups, the one that has a blackened graphite mark on the bottom.
- 2. Turn the laser on to get the system set-up. Remember to change the file name. Once you are ready to start the data acquisition, leave the laser on but cover over the opening so that no light is directed into the calorimeter.
- 3. Start the data acquisition and allow the system to reach thermal equilibrium and a baseline to be established (about 5 min). Remove the covering over the opening and allow for a steady-state thermal signal to be reached (about 8-10 min.).
- 4. Cover over the calorimeter top so that the light is not reaching the inside of the calorimeter. Allow for a baseline to be established (about 5 min). **Repeat** the above **twice more**.

Experiment 3: Thermal Titration of a Saturated Solution of Tris (hydroxymethyl) aminomethane (THAM), C(CH₂OH)₃NH₂, with 3M Hydrochloric Acid

- 1. In a vial prepare 10-12 mg of dried $C(CH_2OH)_3NH_2$ (THAM) in a saturated solution, and position the vial in the sample aluminum cup.
- 2. Fill a 1 ml syringe with the titrant, 3M HCl. Secure the syringe in the sliding top in the usual manner. Lower the tip of the syringe into the vial. Tighten all screws and put the insulating box on the calorimeter.
- 3. Allow the system to reach thermal equilibrium. Start logs and record the signal for a few minutes. Deliver one drop of the titrant. This will produce an exothermic signal.
- 4. Wait for the signal to return to the baseline and deliver another drop. Repeat this until the endpoint of the titration is reached. Once the endpoint is passed small peaks are still observed and may be due to the heat of dilution of the HCl.

Experiment 4: Insect Metabolism

- 1. Remove the insulating top of the calorimeter. **Gently** place a small size insect into the sample aluminum cup. A small glass vial or watch glass may be used as a lid to keep the insect in the aluminum cup.
- 2. Put the insulating box on the calorimeter and allow the system to reach thermal equilibrium before you begin recording the data. Sometimes, it is a challenging task to keep the insect awake. Since the environment inside the calorimeter is

cold and dark, the insect may fall asleep. Find a way to wake up the insect (use of chemicals and other torture methods are not allowed).

- 3. Once the log is started, the recorded thermal signal will show a baseline metabolism of the insect and peaks corresponding to activity events.
- 4. Record the thermal signal for about 15 min. to accumulate thermal signals from the base metabolism and activity peaks.

Experiment 5: Heat of Water Adsorption on Zeolites

- 1. Place a few of these spheres (5-8 or more) in a special 2-drop calorimeter vial and put the vial in an oven for a day or longer. This drying procedure should drive off all water molecules.
- 2. Remove the zeolites from the oven immediately covering the container with a piece of aluminum foil. It is essential to have a tight seal so that no water is absorbed prematurely.
- 3. Measure the mass of the vial, containing the dry spheres, and sealed with Al foil. Place the vial containing the zeolites on a heat sink and leave it there until the vial reaches room temperature. To speed up the cooling you may use some ice, but keep in mind the zeolites should be **at** and **not below** room temperature when they are placed in the aluminum cup.
- 4. Mount a glass tube in the sliding top. Align the tube above the sample aluminum cup. Lower the glass tube into the aluminum cup. Make sure the tube does not touch the bottom or the sides of the aluminum cup.
- 5. Place a small beaker of water on the heat sink before putting the insulating box on the calorimeter. Wait a while to ensure thermal equilibrium as well as a water saturated atmosphere inside the insulating box.
- 6. Start logs and wait a few minutes before removing the Al foil on the vial. Remove the Al foil and immediately, using a paper funnel, slide the zeolites through the glass tube into the aluminum cup. Raise the glass tube carefully without moving it sideways. If you leave the glass tube in place, it may obstruct the flow of water vapors into the aluminum cup.
- 7. Place the aluminum foil back on the empty vial and measure its mass one more time. Use this and the previous mass measurement to obtain the mass of the dry zeolite spheres.

Data Analysis

1. Preparation of Data.

- a. Open a file (e.g. calibration) in Excel. The format is an ACSII file. We want the default options so when the dialogue box comes up, you can click on finished.
- b. Column A is the recorded voltage signal. Click on A to highlight it and then right click. Insert a column. The voltage data moves to column B.
- c. In column A insert the time, 1 second intervals.
- d. Repeat for each of the files that you will be using when you work on that data.

2. Calibration. Open the data in GRAMS 32. There should be a shortcut on the desktop, if not, go to Programs - Galatica – GRAMS 32. Follow the additional instructions about opening the file in GRAMS. Use the "Applications" and "Integration" functions. For the calibration, the **height** (depth) information will be shown on the right hand side. Determine the calibration coefficient, ε , in W/V, using Eqn. 10. For your lab write-up prepare a graph from the calibration by plotting the thermal signal (V) vs. time (s). The graphs for the lab report can be finished on your own. It is more crucial to get the GRAMS information while in the lab period. In a data table, show the battery voltage, the resistor's resistance, and the three height values (volts), their average and standard deviation.

3. Enthalpy of Vaporization. Determine the mass and then the moles of the organic solvent used in each drop. Open the data in Excel, insert a time column and again follow the instructions for opening the file in GRAMS. **Integrate** and **record the area** under each curve to get the total heat, Q, in Joules. Show the area for each peak in a table (v*s). Take the average, to get the mean value for one drop. Using the sensitivity factor, ε (W/V), from the calibration experiment convert the thermal signal (U_{volts}) to thermal power (W). This integrated signal now multiplied by ε is the heat of the evaporation (Q). Use, Q / mol, to determine the Δ_{vap} H. Finally, compare the enthalpy to the literature value (e.g. from the CRC online). In the lab report, include a graph of the volts versus time (or power versus time).

4. Heat of Laser Light Absorption. Open the data in Excel and follow the attached procedure for opening the data in GRAMS. Integrate and record the height (volts) (depth) of each heating event. Take and average to get the mean light absorbed in the aluminum cup. Show the height of each peak in a table. Using the sensitivity factor, ε , from the calibration experiment, once again, convert the average thermal signal to thermal power (W). Compare this with the stated power output from the laser. Calculate the percent absorbed in the aluminum cup and the remaining amount that was reflected.

5. Thermal Titration. Determine the moles of THAM used in the titration. Open the data in Excel and follow the attached procedure for opening the data in GRAMS. Integrate and record the **area** of each exothermic peak. Show these values in a table (v*s) and add the values to get the **total** thermal signal from the reaction. Convert the

thermal signal (V) to thermal power (W) by using ε . These integrated values are now the heat of the reaction (Q) Determine the ΔH of the reaction. Compare this experimental value with a literature value for the reaction. You may have to use Hess's Law and the heats of formation to calculate a literature value for the heat of reaction. In your report show a plot of the thermal signal versus the time as you prepared in the preceding parts.

6. Insect Metabolism. Follow the above procedure for opening the data in Excel and then in GRAMS to integrate the peaks. Because the thermal signals are much smaller in magnitude, work with a small portion of the data, one that has a substantial peak(s). Record the **areas** under the peaks chosen. These are due to heat given off by the insect's metabolism. Show these values in a table (v*s) and sum them. Use ε to convert the values to power (W). These integrated values multiplied by ε are now the heat given off by the insect (Q). Use Hess's Law to calculate the Δ_r H of glucose(C₆H₁₂O₆) combustion. Using the calculated Δ_r H and the heat measured from the peaks, find the mass equivalent that would be used to evolve the experimental amount of heat, *Q*. Convert to this value of glucose to milligrams.

7. Heat of Water Adsorption on Zeolites. Follow the above prodecure for opening the data in Excel and then in GRAMS. Convert the thermal signal (V) to thermal power (W) and graph the data. Integrate to get the total heat, Q. Use the mass of zeolites used to find the moles. Determine the $\Delta_{adsorption}$ H for the selected time period.

Questions and Further Thoughts

1. When analyzing the vaporization graphs, because the volume of organic solvent released in one drop is highly reproducible, the area under the peaks should be the same. However, you may notice that the peaks have broadened. In analyzing the environment of the calorimeter, what may be some reasons accounting for this peak broadening?

A large percentage of the $\Delta_{vap}H$ is used in breaking the intramolecular bonds. What fraction of the $\Delta_{vap}H$ of the organic solvent is spent on expanding the gas vapor? (Assume ideal behavior.)

 $\Delta_{vap}H = \Delta_{vap}U + \Delta_{vap}(PV)$ where volume _{liquid} << volume _{vapor}

2. The experimental value of the $\Delta_{vap}H$ of each of the organic solvents is compared with the literature value and assumes that the experimental value is measured at room temperature, 25°C. Many times however, the lab temperature fluctuates according to the outside temperature. If the temperature in the lab is 18°C, how will this affect the evaporation process. What steps should be included in the calculation to account for this temperature change? Calculate the $\Delta_{vap}H$ of one of the organic solvents at 18°C. What is the percent difference? 3. The time constant, τ , is the thermal response time of the calorimeter. The Tian equation takes into account the heat content of the sample and holder cup:

$$P = \varepsilon (U + \tau^* \mathrm{d}U/\mathrm{d}t)$$

Because the reactions performed in these experiments are slower reactions, the time constant is considered negligible and we calculated the heat flow rate as:

$$P = \varepsilon * U$$

If we had taken the time constant into account, how would this have changed the results of the integrated peaks? Why does the time constant need to be accounted for in a fast reaction taking only milliseconds?

4. If you were constructing a calorimeter for long-term studies on insects, what factors would have to be taken into consideration?

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α	Wave phase shift in quartz
α	Transition region in glassy materials, gradual main chain relaxation
α	Linear coefficients of thermal expansion, (length/(length * °C))
α	Coefficient of expansion of an ideal material
$\alpha_{\rm G}$	Coefficient of expansion of a glass
aadsorbate	Vapor activity of gaseous adsorbate
ac	Alternating current
a _c	Shift factor used to describe the diluent concentration effect on the polymer modulus
a_t	Temperature shift factor for WLF equation
a_w	Water vapor activity
A	Area
Å	Angstrom
AFM	Atomic force microscope
A _{SAW}	kHz change in frequency due to a 1°C change per kHz of coating on resonator surface
AT	Temperature compensated cut of quartz, 35°15' off of Y axis
β	Transition region in glassy materials, relaxation of side groups
β'	Plasticizing parameter relating the diluent volume fraction to the free volume
В	Constant in WLF equation, close to unity
BT	Temperature compensated cut of quartz
BET	Sorption isotherm model by S. Brunauer, P.H. Emmett, and E. Teller
BVD	Butterworth Van Dyke equivalent electrical circuit
δc	Concentration gradient
c _m	Elasticity
c_q	Complex shear modulus of quartz
c_q^{0}	Storage shear modulus of quartz
С	Sensitivity constant for a 5 MHz QCM, 56.6 Hz $\mu g^{-1} cm^2$
С	Capacitance
С	D'Arcy and Watt constant proportional to the number and affinity of weak binding sites
C _p	Heat capacity
C_0	Shunt capacitance or static capacitance, gold electrodes of the QCM, wires and clamping

C1	Capacitance of the resonating QCM
C1	Universal constant for the WLF equation
C2	Capacitance of the added mass to the QCM
C2	Universal constant for the WLF equation
CS	Conformation substate
Cs	Concentration of analyte in the sorbent phase, thin film
C_v	Concentration of analyte in the vapor phase
δ	Transition region of glassy materials, characterized by local motions
δ	Angle of phase shift between the applied stress and the resulting strain
δ	Acoustic wave decay length
tan δ	Tangent of the phase angle, ratio of the storage and loss c omponents
D	Diffusion coefficient
D	D'Arcy and Watt constant proportional number of multilayer binding sites
DAQ	Data aqcuisition board
dc	Direct current
dq/dt	Heat flux
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
e	Piezoelectric constant of quartz
e(T)	Seebeck coefficient
ϵ_{q}	Permittivity of quartz
ε	Calibration coefficient of the thermopile
Es	Seebeck voltage
Е	Internal energy
EF	Equilibrium fluctuations
Endo	Endothermic
Exo	Exothermic
dE_{s}	Change in Seebeck voltage
ΔE_2	Energy change in the thin film adsorbent
f	Oscillation frequency
f	Fractional free volume
$\mathbf{f}_{\mathbf{h}}$	Fraction of heat flow that does not pass through the thermopile
\mathbf{f}_{g}	Fractional free volume at T _g

f _o	Series resonant oscillation frequency
\mathbf{f}_2	Polymer free volume
$f_{ m r}$	Resonant frequency
Δf_s	Frequency shift of the sorbent phase before vapor sorption
Δf_v	Frequency shift of the sorbent phase due to vapor sorption
F	Force
FIMS	Functionally Important Motions
γ	Strain in an elastic deformation
γ	Transitions characterized by bending and stretching motions
γ	D'Arcy and Watt constant proportional to water affinity of the multilayer binding sites
$\gamma_{ m o}$	Maximum strain in an elastic deformation
γ'	Elastic deformation in-phase strain
γ"	Elastic deformation out-of- phase strain
$\gamma^{}$	Elastic deformation complex strain
ΔG	Gibbs free energy
$\Delta_{mixing}G$	Free energy of mixing
$\Delta_{sorption} G$	Free energy of sorption
G	Conductance
G	Complex shear modulus (of a thin film)
G'	Storage shear modulus
G"	Loss shear modulus
G _c	Thermal conductance per thermocouple plate
G _c	Crystal conductance
GC	Gas chromatography
GPIB	General purpose interphase board
G_q	Complex shear modulus of quartz
G_s	Source conductance
Gt	Total conductance
η	Viscosity
η_{f}	Viscosity of the thin film
η_{q}	Viscosity of quartz
h	g H ₂ O/ g lysozyme
h	gadsorbate/gadsorbent
$\mathbf{h}_{\mathbf{f}}$	Thickness of the thin film

$\mathbf{h}_{\mathbf{q}}$	Thickness of quartz	
h'p	Constant in the D'Arcy Watt sorption isotherm	
Н	Enthalpy	
ΔH	Enthalpy change	
$\Delta_{adsorption}H$	Enthalpy of adsorption	
$\Delta_{condensation}H$	Enthalpy of condensation	
$\Delta_{crystallization}H$	Enthalpy of crystallization	
$\Delta_{dehydration}H$	Enthalpy of dehydration	
$\Delta_{denaturation} H$	Enthalpy of denaturation	
$\Delta_{fusion} H$	Enthalpy of fusion	
$\Delta_{hydration}H$	Enthalpy of hydration	
$\Delta_{mixing}H$	Enthalpy of mixing	
$\Delta_{reaction}H$	Enthalpy of reaction	
$\Delta_{sorption} H$	Enthalpy of sorption	
$\Delta_{vaporization} H$	Enthalpy of vaporization	
HCC	Heat conduction calorimeter	
HEW	Hen egg white	
HPLC	High performance liquid chromatography	
Ι	Current amplitude	
i	Square root of -1	
i.d.	Internal diameter	
IGC	Inverse gas chromatography	
φ	Acoustic wave phase shift	
j	Square root of -1	
J	Current density across the quarts of the QCM	
J	Flux	
κ	Electromechanical coupling coefficient	
k	Thermal conductivity	
\mathbf{k}_1	Proportionality constant used for rate of evaporation in Langmuir isotherm	
\mathbf{k}_2	Proportionality constant used for rate of condensation in Langmuir isotherm	
ka	Rate constant for adsorption	
k _d	Rate constant for desorption	
kq	Wave vector for shear wave in quartz	
Κ	Partition coefficient/ equilibrium constant	

K^2	Quartz electromagnetic coupling coefficient
$K_q^{\ o2}$	Electromechanical coupling factor for lossless quartz
K_q^2	Electromechanical coupling factor for lossy quartz
Kc	Equilibrium constant
K _D	Dissociation constant
Keq	Equilibrium constant
$\lambda_{ m q}$	Wavelength of the propagating acoustic wave in QCM
l and $l_{\rm f}$	Thickness of the thin film
Δl_q	Change in the thickness of the resonating quartz
l_q	Thickness of resonating quartz
L	Inductance
L1	Inductance of the resonating QCM
L2	Inducatance of the added mass to QCM
LCR	Simple circuit consisting of an inductor, capacitor, and resistor
LEM	Lumped element model
LF	Low frequency
Δm	Change in the mass
m	Mass
М	Mass factor in determining $\mathbf{Z}_{\mathbf{L}}$
Mb	myglobin
metMb	metmyoglobin
MFC	Mass flow controller
$m_{p\infty}$	Mass of the film and the sorbed solvent vapor at time infinity
${m_p}^i$	Initial mass of the film and the sorbed solvent vapor
m_p^{t}	Mass of the film and the sorbed solvent vapor at time t
ΔM_q	Change in the mass of resonating quartz
$\mathbf{M}_{\mathbf{q}}$	Mass of resonating quartz
ν	Frequency
n	Number of moles
n	Number of the overtone frequency
n _a	Gas molecules adsorbed per gram of solid
n_q	The ratio of the overtone frequency over the quartz resonant frequency
n_1^{s}	Moles of thin film adsorbent
n_2^{g}	Moles of gaseous adsorbate

Odd integer for the resonator harmonic number
Nuclear magnetic resonance
Oscillating capillary nebulizer
Outer diameter
Instantanous power
Partial pressure
Vapor activity
Saturation vapor pressure
Pressure
Heat flux, thermal power
Phosphate buffer solution
Power generate in quartz crystal
Polydimethylsiloxane
Polyisobutylene
Phase lock oscillator
Polyvinylalcohol
Fraction of monolayer, fraction of surface coverage
Charge
Integral calorimetric heat
Quality factor
Heat
Integral heat of adsorption
Quartz crystal microbalance
Density of thin film
Density of vapor when in liquid phase
Density of quartz
Density of sorbent phase
Electrical resistivity
Acoustic wave reflectance coefficient
Dissipation factor
Radio frequency
Rate of mass uptake
Rotations per minutes
Resistance
Motional Resistance
Ideal gas law constant

ΔR	Change in motional resistnace
RH	Relative humidity
R 1	Resistance of the resonating QCM
R2	Resistance of the added mass to the QCM
σ	stress in an elastic deformation
$sub-T_g$	Sub-glass transition, β , δ , γ relaxations
ΔS	Entropy
$\Delta_{mixing} S$	Entropy of mixing
$\Delta_{sorption} \ S$	Entropy of sorption
$\Delta_{vaporization} S$	Entropy of vaporization
S	Sensitivity constant of a thermopile
SAW	Surface acoustic wave device
\mathbf{S}_{exp}	Experimental thermopile sensitivity
\mathbf{S}_{id}	Ideal thermopile sensitivity
τ	Time constant in Tian equation
τ	Average time of stay of vapor molecule on the film surface
t	Time
Т	Temperature
TA	Thermal analysis
T _c	Critical temperature
TCP	Thermocouple Plate
T_d	Temperature of denaturation
T_{g}	Glass transition temperature
TG	Thermogravimetry
TGA	Thermogravimetric analysis
TLM	Transmission line model
T_{m}	Temperature of melt
TSM	Thickness shear mode resonantor
U	Voltage
V	Acoustic factor in determining $\mathbf{Z}_{\mathbf{L}}$
v_1	Volume fraction of diluent
V	Voltage
V	Volume
V ^o	Specific volume at absolute zero
$V^{o}{}_{L}$	Specific volume extrapolated from the liquid state to absolute zero
V^{o}_{G}	Specific volume extrapolated from the glassy state to absolute zero

V_{f}	Free volume
VI	Virtual instrument
$\mathbf{V}_{\mathbf{q}}$	Speed of the propagating acoutic wave in QCM
$\mathbf{V}_{\mathbf{s}}$	Volume of the adsorbent polymer phase
\mathbf{V}_{t}	Specific volume (cc/g)
$V_{\rm v}$	Volume of the adsorbate liquid vapor
VCO	Voltage controlled oscillator
ω	Angular frequency = $2\pi v$
W	Uptake of adsorbate in D'Arcy and Watt isotherm
WLF	Williams-Landel-Ferry equation
W_{m}	Proportionality constant proportional to the energy of adsorption
Х	Displacement
δx	Diffusion direction
\mathbf{X}_1	Thin film adsorbate
X_2	Gaseous adsorbent
X _C	Capacitive reactance
${ m X_{f}}$	Reactance of the thin film
X_L	Inductive reactance
Y	Admittance
\mathbf{Y}_{EL}	Electrical admittance
Z	Ratio of acoustic impdance in quartz over that in the thin film
Z	Thermoelectric material property, figure of merit
Z_{AB}	Complex electrical input impedance
Z_{eq}	Acoustic impedance of QCM
$\mathbf{Z}_{\mathbf{L}}$	Complex acoustic impedance due to the mass loading
Z _L p, Z _L '	Real part of acoustic load impedance
Z _L pp, Z _L ''	Imaginary part of acoustic load impedance
$\mathbf{Z}_{\mathbf{m}}$	Total motional impedance in an equivalent electrical circuit
Zq	Acoustic impedance of quartz
\mathbf{Z}_1	Motional impedance of the unperturbed quartz crystal
\mathbf{Z}_2	Complex motional impedance created by an acoustically thick film

Appendix C. Quartz Constants

(Lucklum et al., 1997; Lucklum & Hauptmann, 1997; Lucklum & Hauptmann, 2000)

$\rho_q = 2.651 \text{ x } 10^{+3} \text{ kg m}^{-3}$	density
$\epsilon_q = 3.982 \text{ x } 10^{-11} \text{ A}^2 \text{s}^4 \text{kg}^{-1} \text{m}^{-3}$	permittivity
$e_q = 9.53 \text{ x } 10^{-2} \text{ A s m}^{-2}$	piezoelectric constant
$\eta_q = 3.5 \text{ x } 10^{-4} \text{ kg m}^{-1} \text{s}^{-1}$	viscosity
$c_q = 2.947 \text{ x } 10^{10} \text{ N m}^{-2}$	piezoelectric stiffened elastic constant
$v_q = 3347 \text{ m s}^{-1}$	shear sound velocity
$K_q^{02} = \left. e_q^2 \right/ (\epsilon_q c_q)$	electromechanical coupling facto for lossless quartz
$K_q^2 = e_q^2 / [\epsilon_q(c_q + j\omega\eta_q)]$	electromechanical coupling factor for lossy quartz
$L_q = (\rho_q h_q^{3}) / (8Ae_q^{2})$	motional inductance of quartz crystal
$C_o = \epsilon_q(A/h_q)$	static quartz capacitance
$\omega = 2\pi f$	angular frequency
$\alpha = \omega(h_q/v_q)$	wave phase shift in quartz
$Z_q = \rho_q v_q = sqrt(\rho_q c_q)$	specific quartz impedance

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Appendix D. "Fast Three Step Method" Equations Used in TK Solver Model

Adapted equations as entered in TK Solver 4.0, File 3_Step Original Equations in (Behling *et al.*, 1999; Lucklum & Hauptmann, 2001)

Rule
;Fast Three-Step Method for Shear Moduli Calculation from Quartz Crystal Resonator
Measurements
Carsten Behling, Ralf Lucklum, Peter Hauptmann, IEEE 46(6), Nov. 1999, 1431-1438
Lq=(q*hq^3)/(8*Aq*eq); motional inductance of quartz crystal
Zq=sqrt(pq*cq); specific quartz impedance
ω=2*pi()*f
ZLpp=(f/f)*-1*pi()*Zq
$ZLp=(R/(2*\omega*Lq))*(pi()*Zq)$
;M= $\omega^* \rho^* hf$; mass factor
;Using the ZLp,ZLpp from above to get first approx. for G',G" values for approximations
$(G0p,G0pp) = power((,0),-1)*((1/M^2,0)+(1/ZLp,0))*(1/3*M^3,0)*(M,ZLpp)$
;(G1p,G1pp)=power((,0),-1)*(power((-2*M,-ZLpp),2)/power((1-pi()/2,0),2))
(G2p,G2pp) = power((,0),-1)*(-
pi()^2/8*ZLp^2,0)+(0,M*ZLpp)+((pi()/4*ZLp,0)*csqrt(pi()^2/4*ZLp^2,-4*M*ZLpp))
$(G2bp,G2bpp) = power((,0),-1)*((4*M^2,0)/(pi(),-8*M*1/ZLpp))$
(G3p,G3pp)=power((,0),-1)*(power((-2*M,-ZLpp),2)/power((1+3/2*pi(),0),2))
;(G4p,G4pp)=power((,0),-1)*(power((-M,-ZLpp),2)/power((pi(),0),2))
;Using the G',G" values to recalculate the ZL values
;(sqG0p,sqG0pp)=csqrt(0,/G0pp)
;(ZL0p,ZL0pp)=csqrt(ρ *G0p, ρ *G0pp)*ctan(0, ω *hf*sqG0pp)
; (sqG1p,sqG1pp)=csqrt(0,/G1pp)
;(ZL1p,ZL1pp)=csqrt(ρ *G1p, ρ *G1pp)*ctan(0, ω *hf*sqG1pp)
; (sqG2p,sqG2pp)=csqrt(0,/G2pp)
;(ZL2p,ZL2pp)=csqrt(ρ *G2p, ρ *G2pp)*ctan(0, ω *hf*sqG2pp)

Rules (continued)
; (sqG2bp,sqG2bpp)=csqrt(0,/G2bpp)
;(ZL2bp,ZL2bpp)=csqrt(ρ *G2bp, ρ *G2bpp)*ctan(0, ω *hf*sqG2bpp)
;(sqG3p,sqG3pp)=csqrt(0,/G3pp)
;(ZL3p,ZL3pp)=csqrt(ρ *G3p, ρ *G3pp)*ctan(0, ω *hf*sqG3pp)
; (sqG4p,sqG4pp)=csqrt(0,/G4pp)
;(ZL4p,ZL4pp)=csqrt(ρ *G4p, ρ *G4pp)*ctan(0, ω *hf*sqG4pp)
;Iteration process, solving for
;(0,0)=(ZL0p* φ 0,0)-ctan(0,M*(φ 0+((1/3)*(φ 0^3)))); φ ~0
;(0,0)= (ZL1p* φ 1,0)-ctan(0,M*(1-(pi()/2)+(2*1))); $\varphi \sim \pi/4$
;(0,0)=(ZL2p* φ 2,0)-ctan(0,M*(1/((pi()/2)- φ 2))); φ ~ π /2
;(0,0)=(ZL2bp* φ 2b,0)-ctan(0,M*(8* φ 2b/((pi()^2)-(4* φ 2b^2)))) ; φ ~ π /2
;(0,0)=(ZL3p* φ 3,0)-ctan(0,M*(-1-((3/2)*pi())+(2* φ 3))); φ ~ 3/4 π
;(0,0)=(ZL4p* φ 4,0)-ctan(0,M*(-pi()+ φ 4)); φ ~ π

Variables						
Status	Input	Name	Output	Unit	Comment	
		ZLp		Pa*s*m-1	real part of acoustic load impedance	
		ZLpp		Pa*s*m-1	imaginary part of acoustic load impedance	
Guess	.001	φ0			φ~0	
Guess	.77018	φ1			φ~π/4	
	1.4503	φ2			φ~π/2	
	1.4503	φ2b			φ~π/2	
	2.2566	φ3			φ~ 3/4π	
	3.0001	φ4			φ~π	
	1090			kg*m^-3	film density	
	4999000	f		s^-1	series resonant frequency	
	8.5	hf		micron	height of film	
	.002651	q		kg*m^-3	quartz density - Lucklum, Faraday D., 107, 1997	
	2.947E10	cq		N*m^-2	piezoelectric stiffened elastic constant, effective shear modulus of quartz - Lucklum, Faraday D., 107, 1997	
	.0033	hq		cm	effective quartz thickness	
	1.9793	Aq		cm^2	effective quartz area	
	.0953	eq		A*s*m^2	piezoelectric constant- Lucklum, Faraday D., 107, 1997	
	8838.833	Zq		Pa*s*m-1	specific quartz impedance	
	55	f		kHz	change in frequency from resonant frequency	
	250	R		Ohm	change in resistance	
		Lq		henry	motional inductance of quartz	
				s^-1	angular frequency	
		М			Mass factor in equation for ZL	

Variables						
Status	Input	Name	Output	Unit	Comment	
		G0p		Ра	First approximations for	
		G0pp		Pa	shear storage, Gp, and shear	
		G1p		Ра	loss, Gpp, moduli	
		G1pp		Ра		
		G2p		Ра		
		G2pp		Pa		
		G2bp		Pa		
		G2bpp		Ра		
		G3p		Ра		
		G3pp		Pa		
		G4p		Ра		
		G4pp		Pa		
		ZL0p		Pa*s*m-1	Acoustic load impedance	
		ZL0pp		Pa*s*m-1	real ZLp and imaginary ZLpp	
		ZL1p		Pa*s*m-1	as calculated from the first	
		ZL1pp		Pa*s*m-1	approximations of Gp and Gpp	
		ZL2p		Pa*s*m-1		
		ZL2pp		Pa*s*m-1		
		ZL2bp		Pa*s*m-1		
		ZL2bpp		Pa*s*m-1		
		ZL3p		Pa*s*m-1		
		ZL3pp		Pa*s*m-1		
		ZL4p		Pa*s*m-1		
		ZL4pp		Pa*s*m-1		
		sqG0p			square root terms of Gp and Gpp	
		sqG0pp			used to calculate the acoustic	
		sqG1pp			load impedance	
		sqG1p				
		sqG2p				
		sqG2pp				
		sqG2bpp				
		sqG2bp				
		sqG3pp				
		sqG3p				
		sqG4pp				
		sqG4p				

Functions					
Name	Туре	Arguments	Comment		
ctan	Rule	2;2	Tangent of complex argument		
ctanh	Rule	2;2	Hyperbolic tangent of complex argument		
cabs	Rule	2;1	Absolute value or modulus of complex argument		
csqrt	Rule	2;2	Square root of complex argument		
csin	Rule	2;2	Sine of complex argument		
ccos	Rule	2;2	Cosine of complex argument		

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