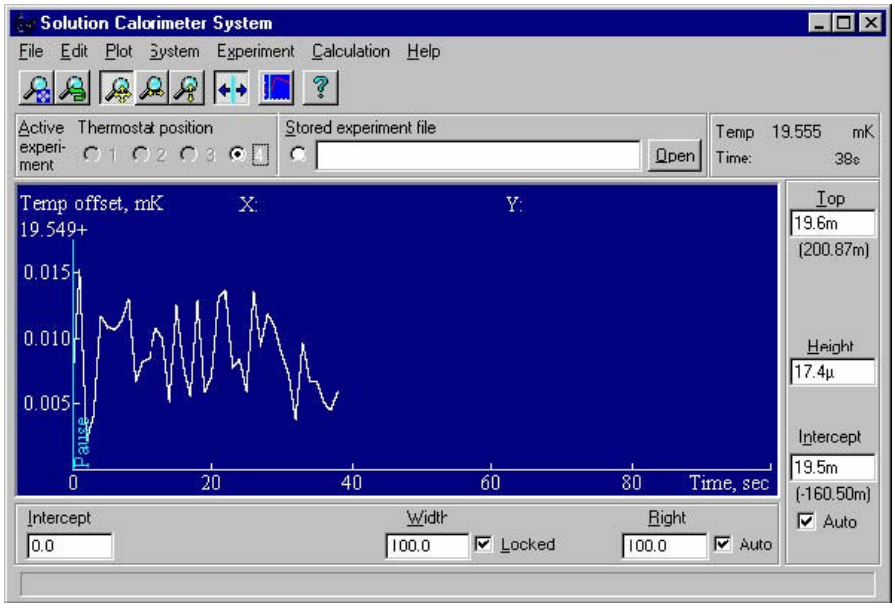
# Operation Instructions for the Precision Solution Calorimeter (SolCal)

The Precision Solution Calorimeter (SolCal) is a semi-adiabatic calorimeter that can be used to measure reaction enthalpy or calculate heat capacity of a sample. Two vessel volumes are available: 25 and 100 mL. This instructional guide will discuss the basics on sample preparation, software, and instrument operation by showing how to perform an electrical calibration for system heat capacity (Cp) verification and Potassium Chloride (KCl) dissolution experiments by using the 100 mL vessel.

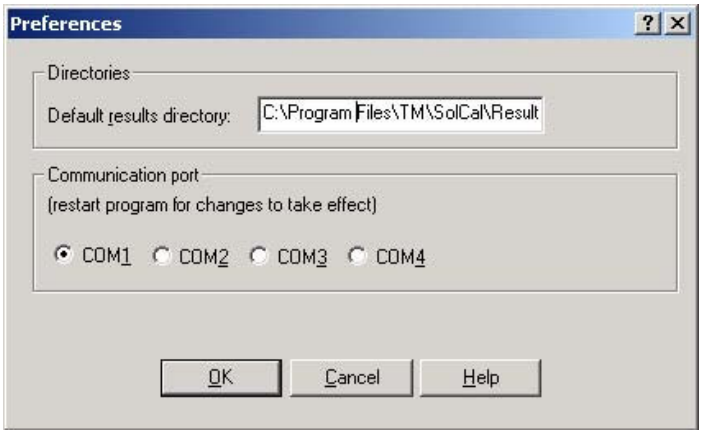
## I. Setting up the SolCal and software for operation

Select **SolCal** from the Thermometric folder under the **Start** button. The **Solution Calorimeter System** form will open. If the communication between SolCal, accessory interface, and computer are correct the SolCal program initiates data collection immediately using an **Empty** experiment method and the screen will appear as below. If no data is being collected upon opening SolCal, communication between SolCal and the computer must be tested (Section Ia).



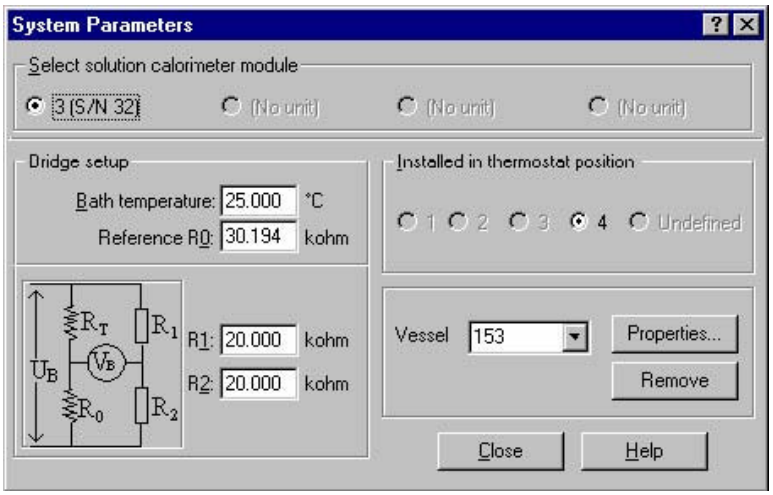

## Ia. Verify the communication between SolCal and computer

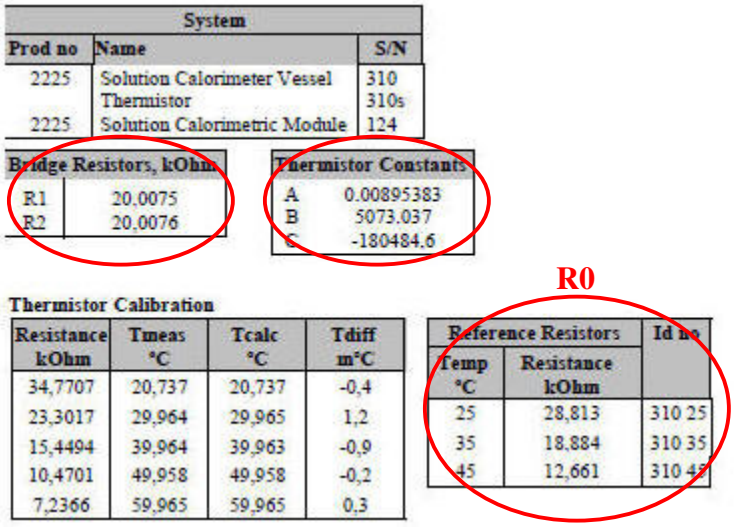
Select **Preferences** from the **File** menu and check that the correct **Communications port (COM)** has been selected for connecting the SolCal to the computer. Click **OK** to continue. Then **Exit** the SolCal program and re-open to test the new communication settings. Repeat this until the correct port is selected and data collection is verified. If communication problems persist please refer to the **Help** menu or contact your local TA Instruments representative.




## Ib. Define the operating temperature of the SolCal

Make sure to end any experiments before opening any selections from the **System** menu or else access may be denied. Select **System Parameters** from the **System** menu and insert the measuring temperature or the TAM set temperature in the **Bath temperature** field. The temperature shown in the SolCal software (i.e. Y-axis) is the offset temperature of the SolCal vessel with respect to the temperature added to this field (25 °C). Check that the serial number of the **Select solution calorimeter module** and the **Installed thermostat position** are correct. The SolCal must have a bridge plug installed for the selected temperature, which refers to resistance **Reference R0**. Check also that the **Reference R1 and R2** and the number of the vessel have been entered correctly into the respective fields. The reference resistance values and vessel number can be found on the documentation that was delivered with the reaction vessel and these values are typically installed into the software prior to delivery. By clicking on the **Properties** button, the thermistor constants that belong to the specific reaction vessel can be inserted. Please again refer to included documentation for verification of the thermistor constant values. DO NOT CHANGE the **Nominal resistance** (50.0000 ohm) and **Lead correction** (60.000 mohm). Please note the units of ohms and milliohms of the nominal and lead corrections, respectively.





| System | | |
|---|---|---|
| **Prod no** | **Name** | **S/N** |
| 2225 | Solution Calorimeter Vessel<br>Thermistor | 310<br>310s |
| 2225 | Solution Calorimetric Module | 124 |

| Bridge Resistors, kOhm | |
|---|---|
| R1 | 20,0075 |
| R2 | 20,0076 |

| Thermistor Constants | |
|---|---|
| A | 0.00895383 |
| B | 5073.037 |
| C | -180484.6 |

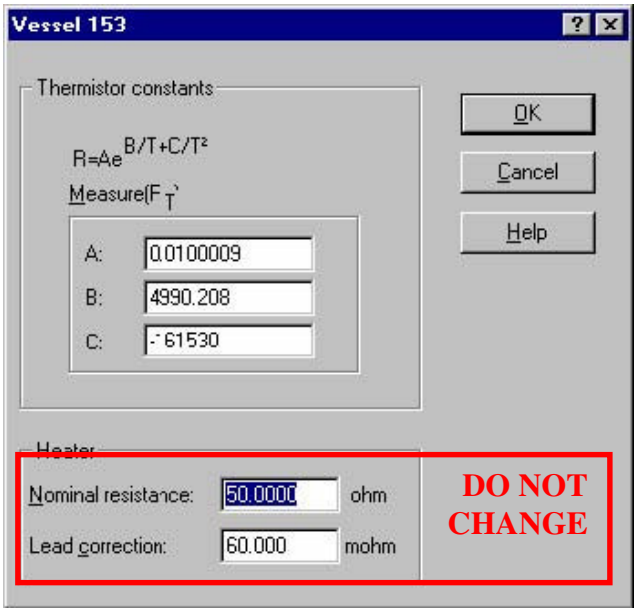
**R0**

**Thermistor Calibration**

| Resistance kOhm | Tmeas °C | Tcalc °C | Tdiff m°C |
|---|---|---|---|
| 34,7707 | 20,737 | 20,737 | -0,4 |
| 23,3017 | 29,964 | 29,965 | 1,2 |
| 15,4494 | 39,964 | 39,963 | -0,9 |
| 10,4701 | 49,958 | 49,958 | -0,2 |
| 7,2366 | 59,965 | 59,965 | 0,3 |

| Reference Resistors | | Id no |
|---|---|---|
| Temp °C | Resistance kOhm | |
| 25 | 28,813 | 310 25 |
| 35 | 18,884 | 310 35 |
| 45 | 12,661 | 310 45 |

Solution calorimeter calibration document delivered with the vessel.



## II. Operational and performance verification of the SolCal

It is common practice to perform at least one Cp verification experiment before running a series of sample or "Break" experiments. During this experiment, a sample can be loaded into the reaction vessel since the heat capacity of the sample can usually be considered negligible compared to the heat capacity of the complete system (i.e. glass vessel, stirrer system, and solvent). During the Cp verification experiment the heat capacity of entire 100 mL system will be calculated. The purpose of this procedure is to verify that the system works properly and reproducible values of the system Cp are calculated. Verification of the heat capacity for the system with 100 mL of water loaded will be described.

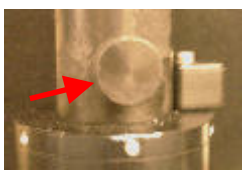
A Cp verification experiment usually consists of three individual heater calibration segments, although a different number of segments can be chosen in the temperature range where linearity is achieved in 'high' resolution mode (i.e. ±230 mK from the set temperature). During a calibration segment, the energy input, calibration power, and time must be defined. The heat input of the calibration segment is selected based on the theoretical experimental heat output. A typical calibration experiment is done by programming three repetitive calibrations of 50 J using water as the solvent. Please refer to Appendix 2 of the Precision Solution Calorimeter manual. See also **Step 1** below.

The heat of solution of KCl when dissolved in water is an endothermic process, which is well suitable for verification and demonstration purposes. Please refer to Section III below and also Appendix 2 of the Precision Solution Calorimeter manual.

**Step 1: Clean and dry the SolCal vessel.** Before filling the reaction vessel with a solvent it should be cleaned with distilled water. Rinse the reaction vessel with water 2 or 3 times and finally add a small portion of acetone. Be sure that no glass pieces or sample remain and the reaction vessel is dry before continuing. Typically, a small vacuum flask connected to a small pump or aspirator together with the silicon tubing (included with SolCal) is used to extract solvent from the vessel. It is strongly recommended not to disassemble the SolCal for cleaning.

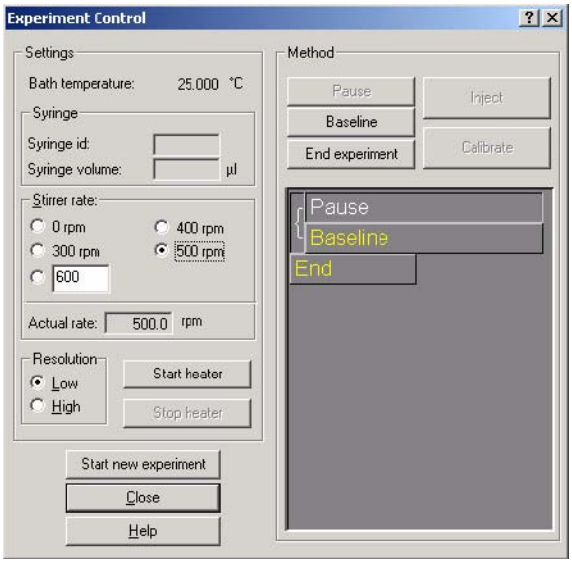
**Step 2: Filling the SolCal vessel.** Use the volumetric pipette provided to transfer the appropriate volume of solvent (e.g. 25 or 100 mL). Leave the SolCal unit it the stand and carefully fill the reaction vessel with the solvent. Avoid touching the walls or bottom of the reaction vessel when immersing the pipette.

**Step 3: Insert the stirrer unit.** Position the stirring unit with or without crushing ampoule down into the SolCal vessel and lock into place using the locking screw. The bottom of the stirrer should be 1-2 mm above the sapphire tip inside the SolCal glass vessel.

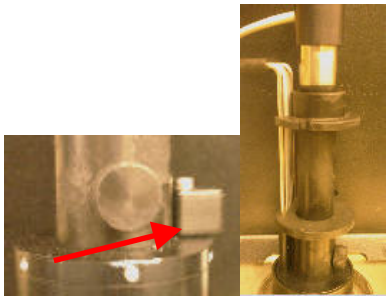


**Step 4: Select Temperature range and initiate stirring.** Select **Experiment Control** under the **Experiment** menu to open the **Experiment Control** form. Select **Resolution** to be **Low** in order to

observe the maximum temperature range of ±2 K. Also set the **Stirrer rate** to 500 RPM.




**Step 5: Equilibration of the SolCal vessel.** The temperature of the reaction vessel will need to be adjusted before lowering the entire unit into the thermostated bath. If necessary, cool the glass vessel filled with solvent to about 1-2 K below the set temperature and then lower into equilibration position. To lower the SolCal into the equilibration position, first rotate the black lever (as shown below) and then place the entire system into the thermostated bath. Allow at least 15-20 min for equilibration of the electronics.



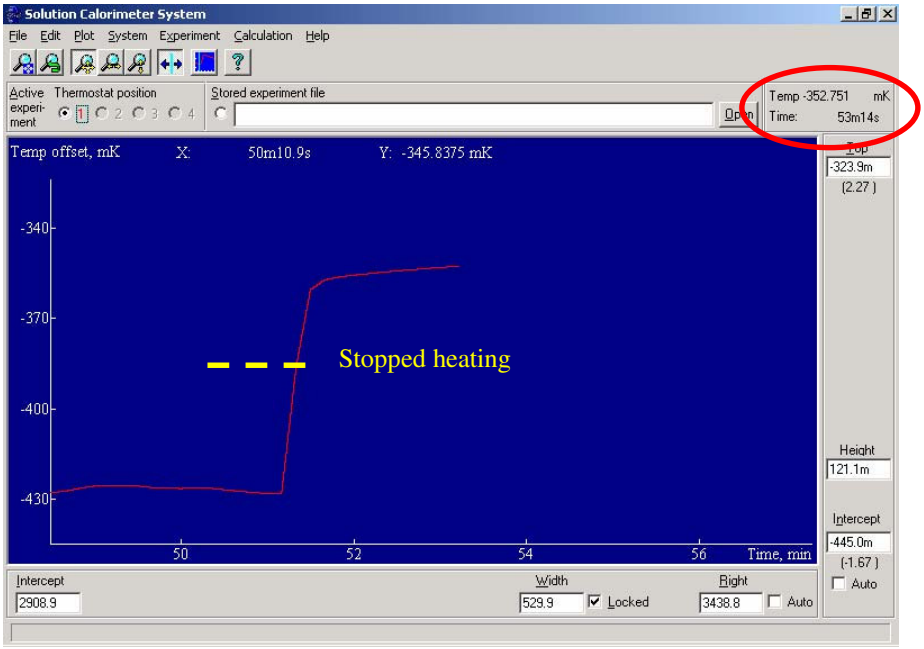
After 15 min, check the temperature of the vessel and make sure it is still below the set temperature in order to allow for the final equilibration and first heater calibration. For example (with water as the solvent), the temperature of the vessel should be lower than –250 mK so to allow temperature drift of final equilibration. Additional heating or cooling may be required before final equilibration (Step 6).

**Step 6: Adjust initial temperature.** This is the most important step of operating a semi-adiabatic calorimeter. Since the first step of every experiment will be a heater calibration, which will emit heat (exothermic), the initial temperature of the SolCal vessel should always be below the set point temperature prior to initiating an experiment.

Close the **Experiment Control** form and observe the temperature in the upper right corner of the screen. When the temperature is reasonably stable within the required temperature range (-400 to -200 mK) rotate the black lever and lower the SolCal unit entirely into the thermostated bath (or measuring position). At this point, another 20-40 min are required for baseline stabilization and this time can be incorporated into the first 'pause' section of an experiment. Thus, the SolCal is ready to perform an experiment.

**IMPORTANT:** At this point the SolCal is in the measuring position and the temperature should be below –200 mK if making a measurement in the 'high' resolution temperature range. It is suggested to perform the Cp validation in 'high' resolution mode, which measures temperatures of ±200 mK. However, for this section keep the SolCal in the 'low' resolution mode so that the real time temperature can be observed. The resolution can be switched to 'high' before initiating an experiment.

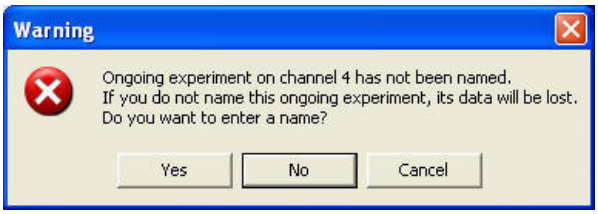
If the temperature is too low, the SolCal vessel must be heated. There are multiple methods of heating the vessel: calibration heater, using gloved hands, or other heating device. The type of heating method to use will depend on the magnitude of the temperature offset. If the temperature reading is –1 to 0 K then the SolCal can remain lowered in the bath and the internal calibration heater can be used (See Steps 11 & 12 below). If the temperature is still colder than –1 K it would be recommended to remove the SolCal momentarily and heat the glass vessel by cupping gloved hands around the glass vessel or using a hairdryer to heat it up above –1 K offset temperature. Please wear powder-less gloves while warming the vessel with your hands. When the temperature reaches the appropriate range, immediately lower the SolCal into the measuring position. This process should take no longer than a minute or two. When applying heat or cold carefully observe the curve on the screen so the change in temperature is moderate. It is very easy to over-shoot the temperature range and adjusting the temperature in small increments will make this process more efficient. In the plot above, the calibration heater was used at full power (500 mW) and was stopped when the temperature reached -390 mK and the actual temperature of the vessel began to level out at -350 mK (see picture above). Please note that the heat capacity of the solvent affects the rate of temperature change and recommendations given here are for an aqueous system.




If the temperature is too high, the SolCal vessel must be cooled. If the temperature is higher than -200 to -100 mK it would be recommended to remove the SolCal momentarily and cool it down. Use an aerosol cold spray or squirt a small portion of acetone on the lower portion of the glass reaction vessel to cool it down. Be careful not to get any acetone on the thermal adhesive on the top of the reaction vessel.

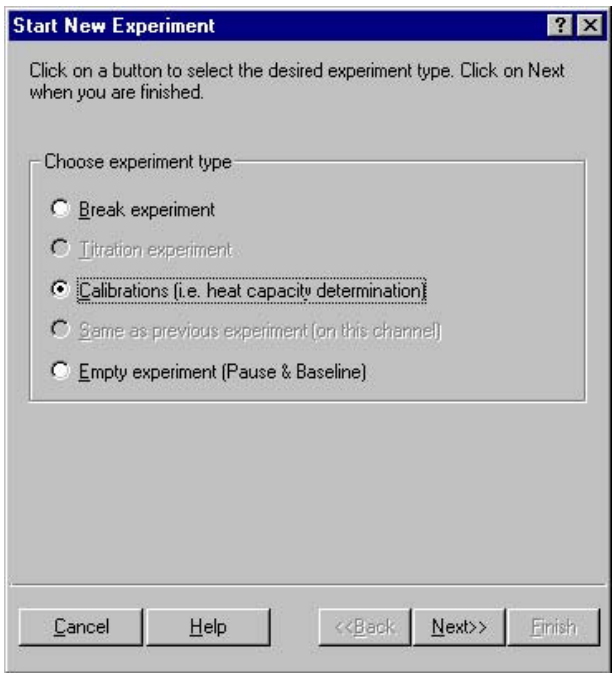
**Step 7: Initiate the Experiment.** Select **Experiment Control** under the **Experiment** menu to open the **Experiment Control** form again. Change the **Resolution** to 'High' to observe the temperature range of ±230 mK. Then click the **Start new experiment** button. End the current experiment by selecting **Yes**.

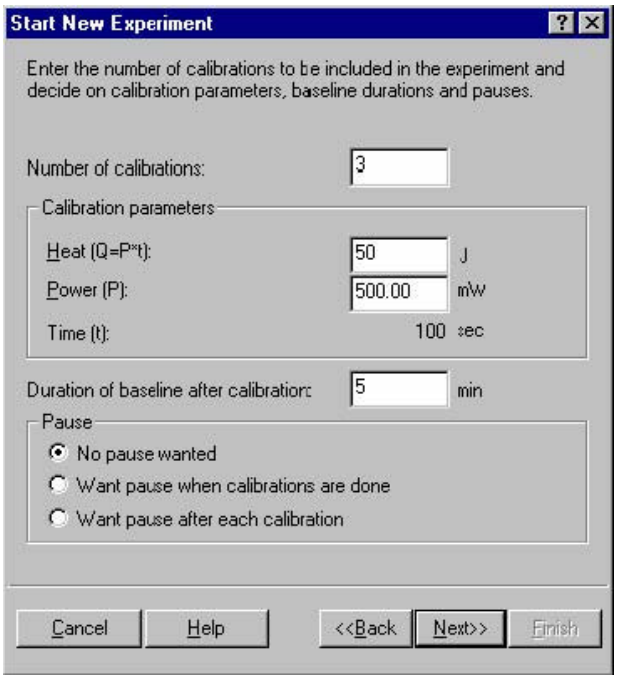

It is not necessary to save this blank experiment or temperature equilibration. In this case, select **No**. If selected Yes, a filename prompt will be requested. The file will be saved in the default location, which is defined under the **File/Preferences** menu.




The **Start New Experiment** form will appear.

**Step 8: Choose experiment type.** Select **Calibrations (i.e. heat capacity determination)** and click **Next**.



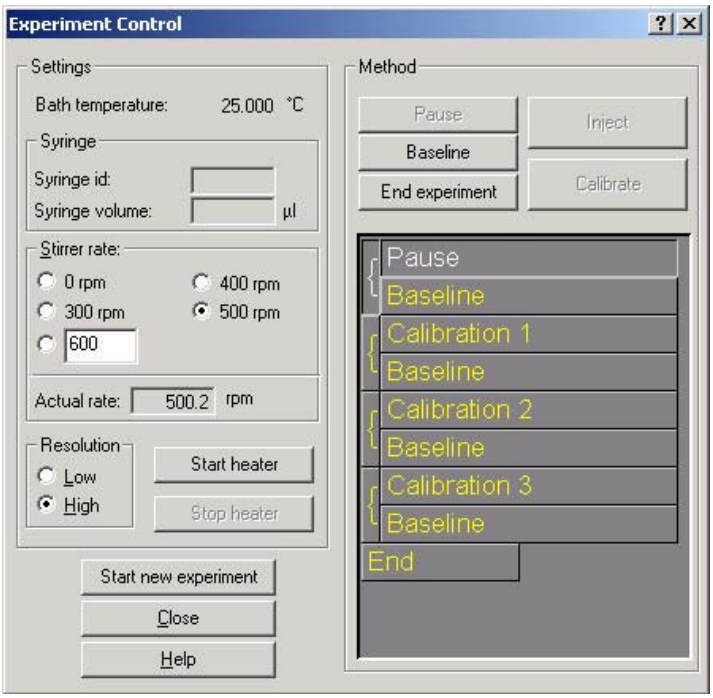




**Step 9: Insert the calibration parameters.** The next form appears and the experimental parameters are to be defined. Select the **Number of calibrations** to 3. When water is used as the solvent, the **Heat** added during each calibration should be 50 J. The **Power** used for adding the heat should be defined to 500 mW (W = J/s), which means that it will take 50 J/500 mW = 100 s to input 50 J into the system. After each calibration a baseline will be recorded. The length of the **Baseline** should be set to 5 min.

A **Pause** section can be monitored after the baseline section of the last calibration or after the baseline sections of each individual calibration. The reason for choosing either option is to give the user opportunity to adjust the length of the baseline section(s) after the experimental data has been collected. This baseline adjustment can be done by using the **Move Events** button. For the calibrations experiment it is not needed, thus select **No pause wanted**.

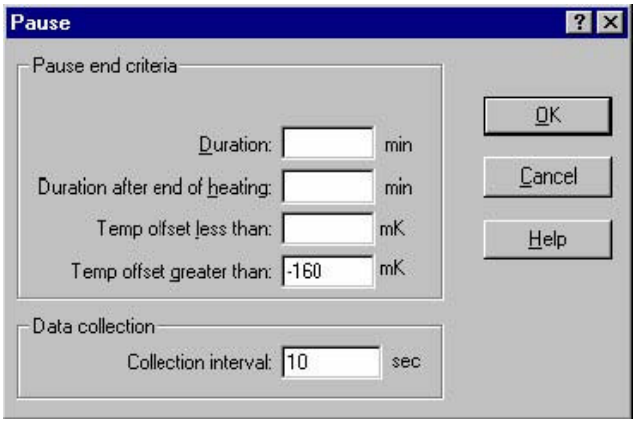
**Step 10: Enter a filename.** Click **Next** to be prompted to enter a filename. The default name includes the type of experiment, the heat added for each calibration, and the date. The file will be saved in the default location, which is defined under the **File/Preferences** menu. Click **Finish** to end the calibration experiment set-up. Data collection for the calibration experiment will start immediately. The **Enter Experiment Control** form will appear again showing all **Sections** included in the experiment.


**Step 11: Initial Pause section.** The end criteria for the initial Pause section of the method must be defined. In this case, the experiment starts with a **Pause** and ends with a **Baseline** before the final **End** section.




Double click the first **Pause** section to open a form where the settings can be entered. For the calibration experiment only the first **Pause** section has to be entered. For this calibration experiment enter -160 mW in the **Temp offset greater than** field.

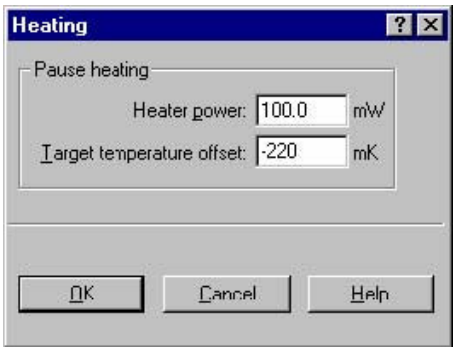
The **Pause** section will end and the experiment will proceed to the next baseline after the temperature of the vessel is greater than -160 mK. **Data collection** is set by default to 10 s in a **Pause** section. It is also possible to define different criteria for each section of the experiment, but these criteria will not be shown here.




**Step 12: Fine temperature adjustment.** At this point the temperature of the vessel should be slightly less than –200 mK. If not, see step 6 above. Click the **Start heater** button to open the **Heating** form. When water is used the **Heater Power** and **Target temperature offset** can be set to 100 mW and -220 mK, respectively. The **High** resolution temperature offset range of SolCal is ±230 mK and all measurements must be performed within this range. Thus, before an electrical calibration is started, the heater is used to heat the system up to a temperature just below the linear range of the high resolution mode. The SolCal should then remain idle except for stirring for approximately 20-40 min to reach the linear temperature where the first baseline will start.

Note that the Target temperature offset value of the heater and that value defined in the Pause section are different. When doing this experiment at 25° C, this difference will allow approximately 40 min to pass as the temperature of the reaction vessel equilibrates from -220 mK to -160 mK before the first baseline section is initiated.

**IMPORTANT:** The linearity of the baseline should be verified before the beginning of the first baseline section. Check Exponential fit is located under the Experiment menu. The Exponential fit should be less than 10 µW before the first baseline begins.





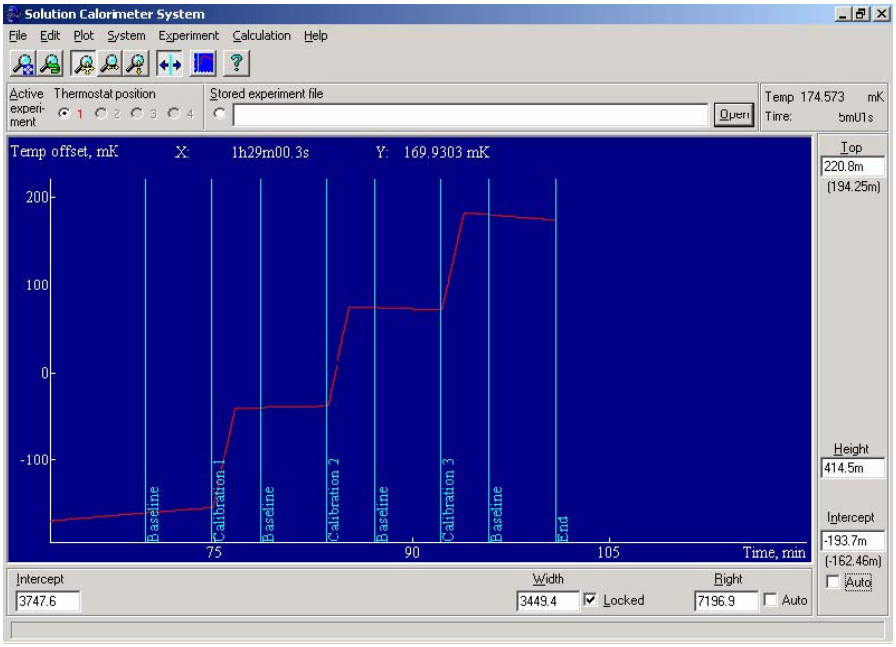
**NOTE:** The **Heater** and **Pause** parameters described have been defined through experience using water as a solvent at 25 °C. When using different temperatures or solvents other than water, these parameters may have to be altered.

Alternatively, the **Pause** can be set to begin after the heater turns off. In addition to the **Temp offset greater than** it is possible to define the **Duration after end of heating** to 40 min. An advantage of using a Duration criteria for the first Pause is that all experiments will start at the same temperature. If preferred, go back to **Step 11** and change the **Pause** criteria. Please note the heater must already be

activated in order to select the duration after heating criteria.

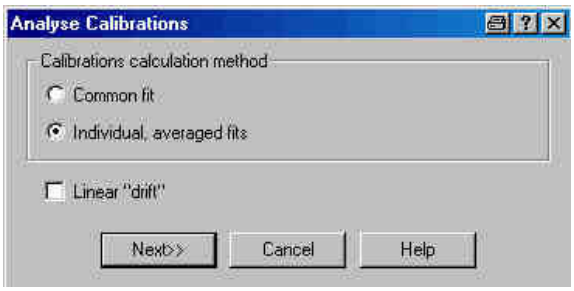
The experiment will now proceed automatically and perform all **Calibrations** and **Baselines.** The **End** of the experiment will be marked on the plot.

**Step 13: End of Experiment.** When the experiment has ended, use the zooming tools located on the tool bar to investigate the experimental curve.

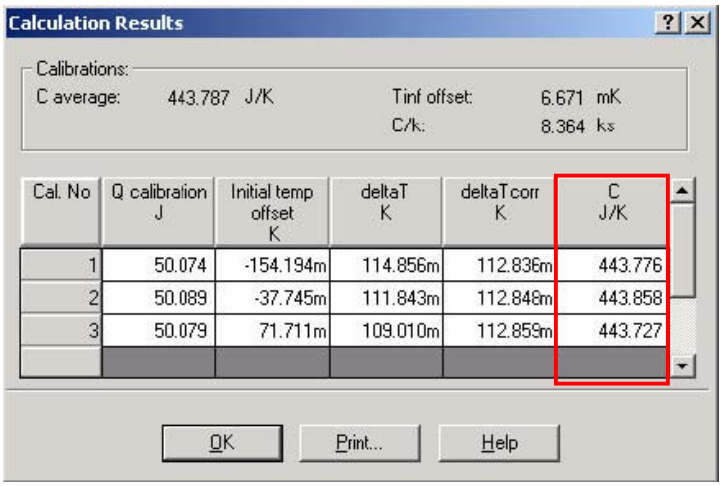



**Step 14: Clean and dry the SolCal vessel.** Before filling the reaction vessel with a solvent it should be cleaned with distilled water. Rinse the reaction vessel with water 2 or 3 times and finally add a small portion of acetone. Be sure that no glass pieces or sample remain and the reaction vessel is dry before continuing. Typically, a small vacuum flask connected to a small pump or aspirator together with the silicon tubing (included with SolCal) is used to extract solvent from the vessel. It is strongly recommended not to disassemble the SolCal for cleaning.

**Step 15: Analyze the experiment.** Select **Analyse Experiment** from the **Calculation** menu. Select **Individual, average fits** and click **Next** to perform the calculation.



The calculated heat capacities (**C**) for the three calibrations are displayed. When using the TAM as the thermostated bath, a standard deviation of ±0.2 J/K between all three values is considered acceptable perofrmance. Click **Print** to print the results. Click **OK** to close the form. In the example below the highest and lowest C values differ by a maximum of 0.131 J/K, which is acceptable.

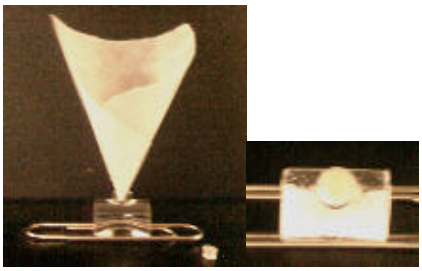


## III. Sample Experiment

If a performance verification has been ended and analyzed as described above, a KCl filled crushing ampoule should already be in position inside the reaction vessel and a sample (or Break) experiment can be initiated directly. If not, a crushing ampoule has to be prepared and loaded into the SolCal using the procedure described Chapter 6 in the Precision Solution Calorimeter instruction manual.

Break experiments are in principle performed in the same way as a heat capacity verification experiment. However, the Break method is slightly different than the Calibration method. In the Break method there is an initial calibration followed by a break section and a final calibration. The pause and baseline sections have been omitted here for simplicity and will be discussed later. The analysis of the results of a Break experiment can be done using two different procedures and the results from both will be displayed.

**Step 1: Preparation of sample.** Use a balance and weigh an empty ampoule and rubber seal. Be observant of static as the glass ampoule mass may not stabilize without proper precautions to prevent static. Then place a known amount of dried KCl (300-500 mg) into a crushing ampoule. Seal the ampoule using the using the tared rubber seal and record an accurate sample mass. Then take the ampoule and seal with melted beeswax that is provided. Please refer also to Chapter 6 of the Precision Solution Calorimeter instruction manual. Another reference for KCl dissolution is NIST SRM 1655.[1]

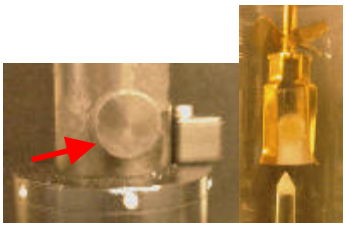


**Step 2**: **Place the sample ampoule in the stirrer unit.** Position the crushing ampoule with sample into the SolCal stirring unit. Be careful not to handle the ampoule by the ends and slide the ampoule up into the stirrer until stopped by the wings.

**Step 3: Clean and dry the SolCal vessel.** See also Steps 1 and 15 in the performance verification section.

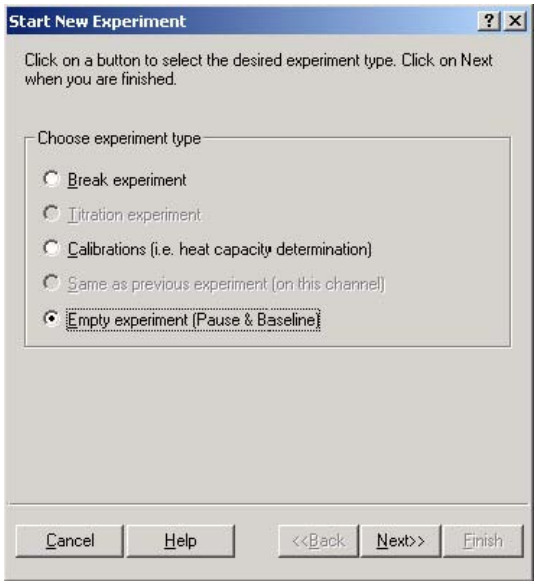
**Step 4: Filling the SolCal vessel.** See also Step 2 in the performance verification section.

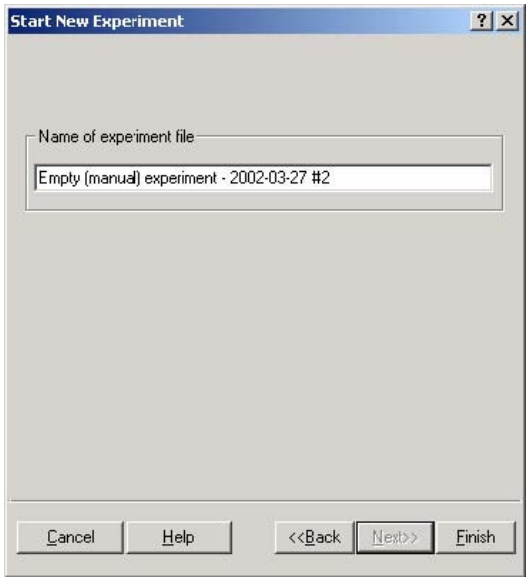
**Step 5: Insert the stirrer unit.** Insert the stirring unit down into the SolCal unit and lock into place using the locking screw. The bottom of the ampoule should be 1-2 mm above the sapphire tip inside the SolCal glass vessel. If not, look to Appendix A of the Precision Solution Calorimeter manual for further instructions on how to adjust the height of the stirrer.



**Step 6: Initiate an Empty experiment**. If a previous experiment has just been ended, SolCal will not collect data and no data will be displayed on the screen. Thus, before initiating a new Break experiment it may be helpful to start an Empty experiment method so that the temperature of the reaction vessel can be monitored. If the SolCal is not already collecting the temperature signal select **Experiment Control** under the **Experiment** menu to open the **Experiment Control** form again. Click the **Start new experiment** button. The **Start New Experiment** form will appear. Select **Empty experiment** and click **Next** to continue. You will be prompted for a file name. Click **Finish** to continue to return to the **Experiment Control** form. No filename for the empty experiment is necessary and can be left as default.

Select **Resolution** to be **Low**. Set the **Stirrer rate** to 500 RPM.




**NOTE:** If an experiment is in progress you will be prompted to end and name the current experiment as described previously.

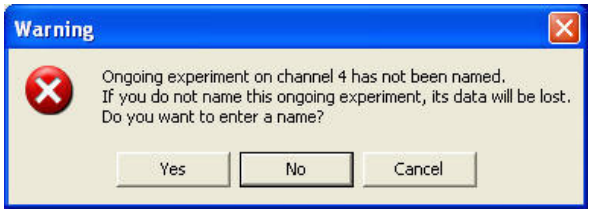
**Step 7: Adjust initial temperature**. The temperature of the glass vessel will need to be adjusted before lowering the entire unit into the equilibration position. See also Step 6 of the performance verification section. Close the **Experiment Control** form and observe the temperature offset for 10-15 min.

If the temperature offset is above -300 mK, the SolCal must be removed from the thermostat and cooled down. Use acetone or some cold spray and gently cool the vessel until the temperature offset is in the range of -400 to -300 mK. If the temperature becomes to cold use a hair dryer or use your hands to heat the reaction vessel slightly until the temperature offset becomes -400 to -300 mK. Before initiating a break experiment the temperature offset of the reaction vessel should be adjusted to be slightly below -300 mK and the SolCal should be lowered into the measuring position.

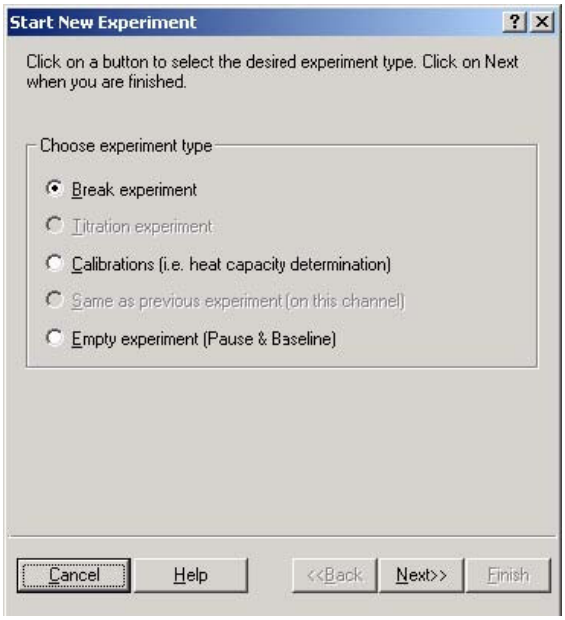
**Step 8: Lower the SolCal and set resolution.** Rotate the black lever and lower the SolCal unit entirely into the thermostated bath (or measuring position). At this point, another 20-40 min are required for baseline stabilization and this time can be incorporated into the first 'pause' section of an experiment.

**Step 9: Initiating a Break experiment.** Open **Experimental Control** and change the **Resolution** to **High**. Then click the **Start new experiment** button and you will be asked to end the current experiment. Select **Yes**.

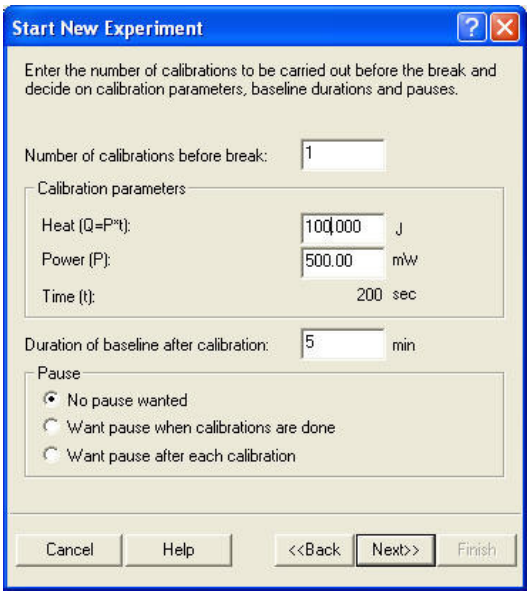

You will be prompted to save the current experiment. In this case, select **No** since you only have initiated an Empty experiment in order to observe the temperature offset.



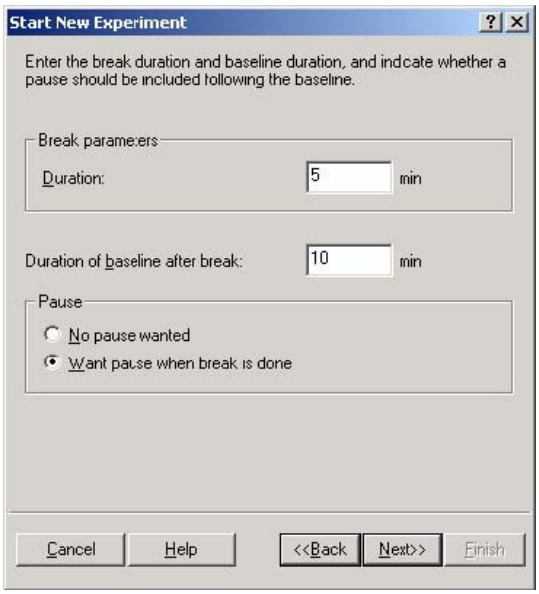

Select **Break experiment** and click **Next** to continue. The parameters of the break experiment must be defined. Select the parameters according to the figures below.



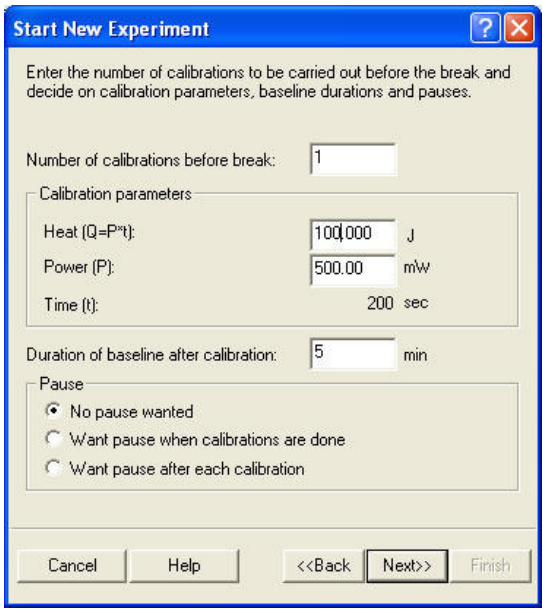

For the first **Calibration** the amount of **Heat** entered should correspond to that expected during the dilution of 400 mg of KCl, which is expected to be approximately 100 J. Maximum heater **Power** of 500 mW has been found suitable for the calibration. A typical **Baseline** is 5-10 min. In a break experiment it may be good practice to collect a **Pause** after each calibration since this option allows you to change the length of the **Baseline** after performing the experiment. Click **Next** to continue.



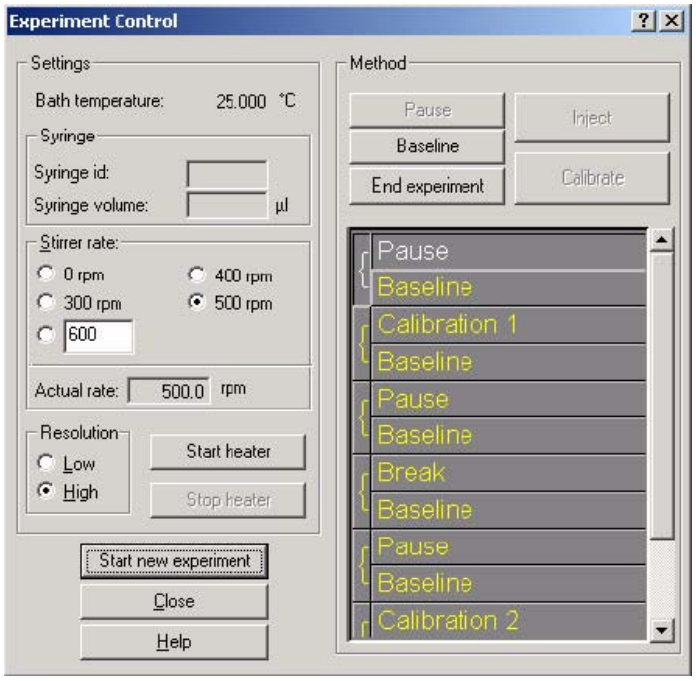

Define the duration for the **Break** section. The time limit depends on the type of experiment being performed. Fast dilution processes only require a short time (5 min), whereas a slower process (or the use of a more viscous solvent than water) might require longer times (10-30 min). By inserting a **Pause** section after the break it is possible to increase the length of the **Break** section in case the dilution process is observed not to complete in the given time. In this experiment, dilution of KCl in water is fast and a **Break** section of 5 min is long enough for the process to complete. A **Baseline** of 10 min should be used after the break.



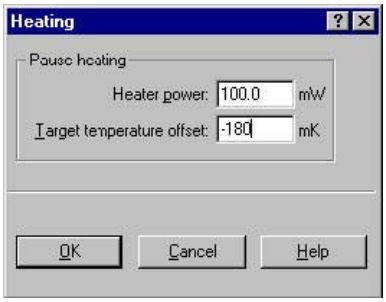

The final **Calibration** after the **Break** should match that of the first calibration. After the final **Calibration** there is no need for a Pause section. Click **Next** to continue.



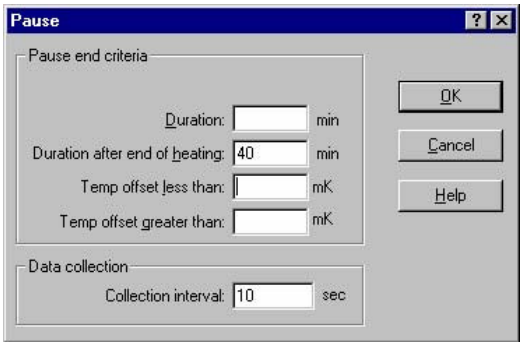

Enter a file name. Click **Finish** to start the experiment. The **Experiment Control** form will appear. The individual sections of the experiments will be displayed. WHITE section(s) have been ended or are in progress whereas YELLOW section(s) are waiting to be performed.



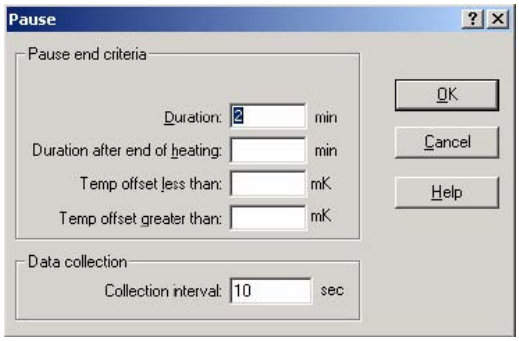

**Step 10: Start the heater.** Click the **Start heater** button and use the settings below. During a break experiment the target temperature can be lowered to take advantage of the linear range of the temperature offset scale and -180 mK is a good choice. The time for the first **Pause** will be defined to 40 minutes after the heater stops in the next section.



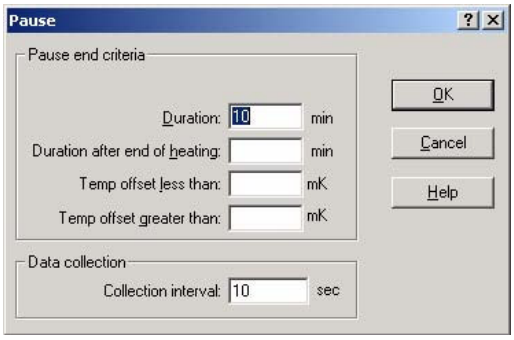

**Step 11: Set the Pause section parameters.** Enter the end criteria for all three **Pause** sections of the experiment. Double click the first **Pause** section and enter 40 min in the **Duration after end of heating** field. When the temperature reaches -180 mK the heater turns off the pause will continue for additional 40 minutes before the experiment proceeds to the next **Baseline** section. During the remaining 40 minutes the temperature offset of the system will slowly increase.



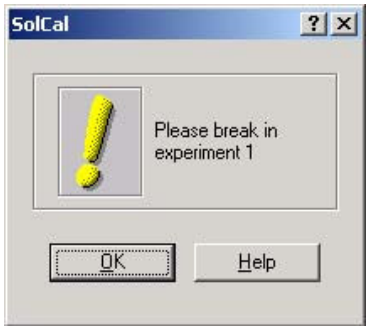
The second **Pause** is defined to **Duration** of 2 min.




The third **Pause** is defined to **Duration** of 10 min. The purpose of this **Pause** is that it can be used to prolong the proceeding **Break** section during analysis (if necessary). Click **Ok** to return to the **Experiment Control** form.

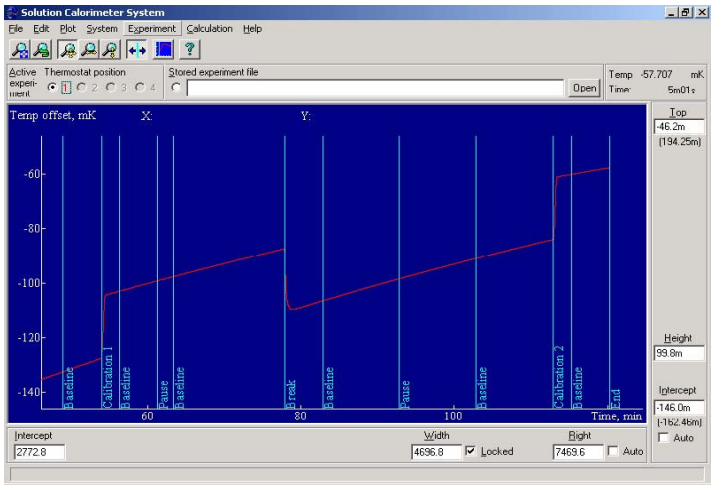



**Step 12: Break the ampoule.** After the first calibration and baselines have been performed a message will appear on the screen that prompts you to break the crushing ampoule.

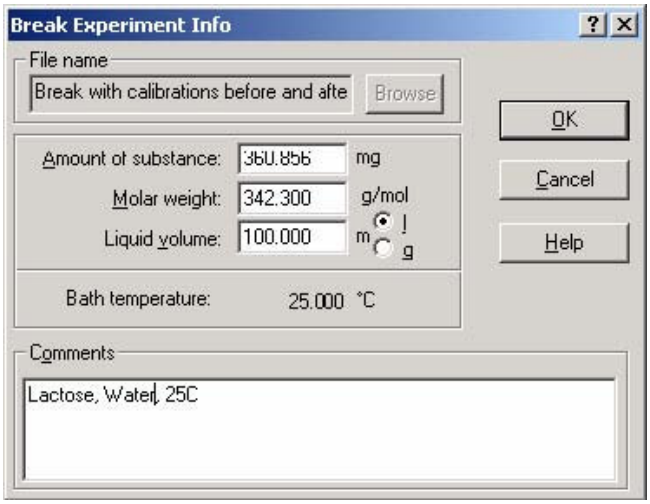



Breaking the crushing ampoule is done by gently pressing the white button on the SolCal in the vertical position. Make sure to press down slowly and steadily until you hit a stop and then release in the same fashion. When the button is pressed a sensor will register that the break has been done and automatically change sections. A mark called 'Break' can be observed on the screen.

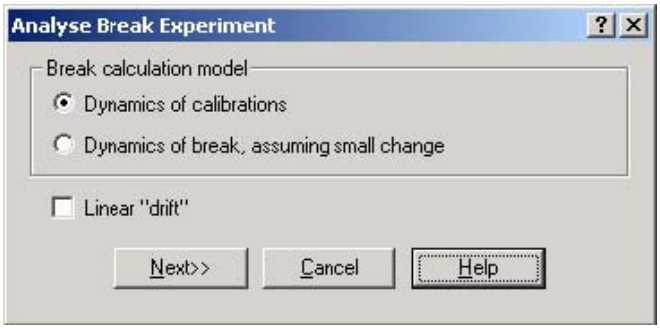
After the **Break** the experiment proceeds automatically until the end. Make sure to enter sample information explained in the next section. The complete graph can be observed on the screen. Use the zooming tools on the tool bar to investigate the experimental curve.

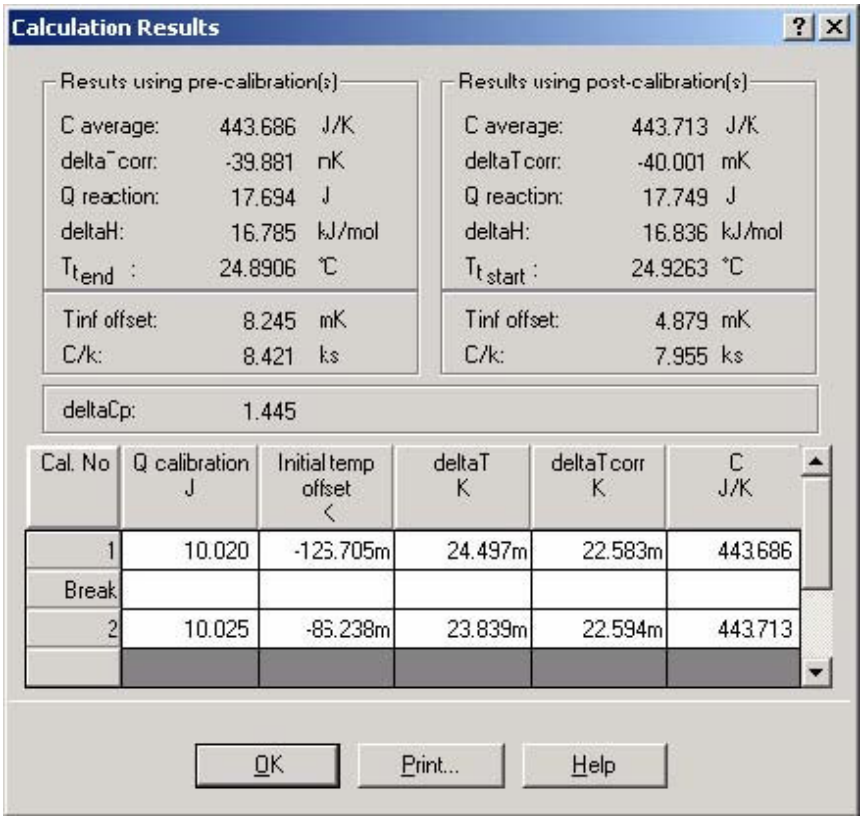



**Step 13: Insert sample information.** Select **Experiment Info** from the **Experiment** menu. The **Break Experiment Info** form will open. Enter the **Amount of substance**, **Molecular weight** (e.g. $MW_{KCl}$ = 74.5513 g/mol), and the **Liquid Volume** of solvent. Select the units for the solvent, **mL** or **mg**. In addition, include any important information to the **Comments** field. For example, sample name, lot number, prehistory, thermostat temperature, and solvent information. Click **OK** to close the form and this information will be saved with the data file.



**Step 14: Analyze the experiment.** Select **Analyse Experiment** from the **Calculation** menu. Select **Dynamics of Calibrations** and click **Next** to perform the calculation. Please refer to Ch. 3 the Precision Solution Calorimeter manual for further information on the 'Dynamics of break' and 'Linear drift' functions.




**Step 15: Clean and dry the SolCal vessel.** Finally, remove the solvent and the glass pieces from the reaction vessel by using the tubing provided connected with a vacuum line to rinse out the water, glass pieces, and sample residue. Rinse the reaction vessel with water 2 or 3 times and finally add a small portion of acetone. Be sure that no glass pieces or sample remain and the reaction vessel is dry before continuing. Typically, a small vacuum flask connected to a small pump or aspirator together with the silicon tubing (included with SolCal) is used to extract solvent from the vessel. It is strongly recommended not to disassemble the SolCal for cleaning.

**References:**

1. National Bureau of Standards (NBS) or National Institute of Standards and Technology (NIST) Certificate, Standard Reference Material (SRM) 1655. Potassium Chloride, KCl (cr) for Solution Calorimetry.