Operating Instruction Manual 593M

6755

Solution Calorimeter

Operating Instruction Manual
For models produced after November 2010

QUICK START

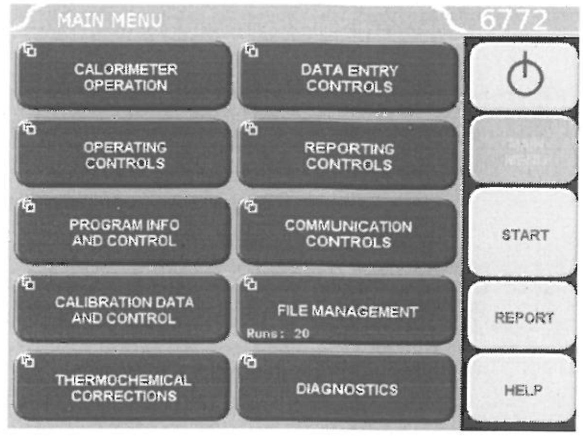
Before starting to use the calorimeter for the first time, it is recommended that the user perform a dry run with the calorimeter completely assembled, but with no liquid in the Dewar and no sample in the rotating cell. This will give the user an opportunity to become familiar with the individual parts of the calorimeter and the manner in which they must be handled. The calorimeter must be standardized prior to analyzing a sample.

1. Allow at least 20 minutes for the calorimeter to warm up.
2. Turn on the stirrer motor switch on the 6755 calorimeter.
3. Prepare and weigh the sample to 0.0001g or 1 mL in the PTFE dish.
4. Fill the Dewar volumetrically or by weight.
5. Install the thermistor probe in the cover opening and press the bushing firmly into place to anchor the probe in its proper position.
6. Lower the cover assembly with the cell and thermistor probe into the Dewar and set the cover in place on the air can, then drop the drive belt over the pulleys, start the motor and press the start key.
7. The pre-period will now start. When the reactants come to thermal equilibrium, the thermometer will beep. Initiate the reaction by pressing downward on the push rod to drop the sample out of the rotating cell.
8. During the reaction period, the enthalpy change will occur.
9. The calorimeter will again come to equilibrium during the post period and at the conclusion of the test, the calorimeter will signal the user and produce a report.
10. Stop the calorimeter motor, raise the cover carefully and wipe any excess liquid from the parts that were immersed in the Dewar. Remove the thermistor probe from the cover and remove the sample dish from the end of the push rod; then remove the rod and release the glass cell from the drive shaft.
11. Lift the Dewar out of the air can and empty it. Wash and dry all wetted parts carefully.
12. At the end of the testing period, turn OFF the thermometer at the power switch.

OPERATION

Menu System

All configurations and operations are handled by a menu-driven system operated from the bright touch screen display. The settings and controls are organized into eight main sections as displayed on the MAIN MENU.



Note:

Keys with a "double box" in the upper left hand corner lead to sub-menus.

Menu Keys

The controls that change the data field information in the menus will be one of the following:

1. **Toggles.** These data fields contain ON/OFF or YES/NO choices. Simply touching the key on the screen toggles the choice to the other option. The current setting is displayed in the lower right corner of the key.
2. **Option Selection.** These data fields contain a list of options. Touching the key on the screen steps the user through the available choices. The current setting is displayed in the lower right corner of the key.
3. **Value Entry Fields.** These data fields are used to enter data into the Calorimetric Thermometer. Touching the key on the screen brings up a sub-menu with a key pad or similar screen for entering the required value. Some keys lead to multiple choices. Always clear the current value before entering a new value. Once entered the screen will return to the previous menu and the new value will be displayed in the lower right corner of the key.
4. **Data Displays.** Most of these keys display values that have been calculated by the Calorimetric Thermometer and are informational only. Certain ones can be overridden by the user entering a desired value through a sub-menu. The value is displayed in the lower right corner of the key.
   Note:
   Some keys will respond with an opportunity for the user to confirm the specified action to minimize accidental disruptions to the program and/or stored data.

Control Keys

There are five control keys which always appear in the right column of the primary displays. These keys are unavailable when they are gray instead of white.

1. **Escape.** This key is used to go up one level in the menu structure.
2. **Main Menu.** This key is used to return to the main menu touch screen from anywhere in the menu structure.
3. **Start.** This key is used to start a Calorimetric Thermometer test.

4. **Report.** This key is used to access the test results stored in the Calorimetric Thermometer, to enter thermochemical corrections, and to initiate a report on the display, printer or attached computer.
5. **Help.** This key is used to access help screens related to the menu currently displayed on the touch screen.
6. ⏻ This key appears in the Escape key location when the main menu is displayed. This key is used to shut down the calorimeter program before turning off the power.

Programming

The program in the 6772 Calorimetric Thermometer can be extensively modified to tailor the unit to a wide variety of operating conditions, reporting units, laboratory techniques, available accessories and communication modes. In addition, the calculations, thermochemical corrections and reporting modes can be modified to conform to a number of standard test methods and procedures. Numerous provisions are included to permit the use of other reagent concentrations, techniques, combustion aids and short cuts appropriate for the user's work.

Note:
Changes to the program are made by use of the menu structure. Any of these items can be individually entered at any time to revise the operating program.

Default Settings

The 6772 Calorimetric Thermometer is preprogrammed with default settings for use with the 1341 Plain Jacket Calorimeter. On the operating controls page of the 6772 Thermometer is the Method of Operation key. This key toggles the thermometer between solution and combustion calorimetry. **Make sure that the calorimeter is set to solution calorimetry.** This will force the calorimeter to restart and bring up the appropriate set of menus and eliminate all of the keys dedicated to combustion calorimetry.

The default values of the 6772 are designed to operate with the 1341 Plain Jacket calorimeter. Therefore, **the following parameters must be changed in the Calorimetry Parameters menu found in the Diagnostics Menu.**

Correction (K) Parameters:

K1	0.5
K2	0.00080
K3	1.0
K4	0.0
K5	0.0

Blackout (B) Parameters:

Misfire Blackout (B2)	72
Derivative Blackout (B3)	0.5
Dynamic Blackout (B4)	6
Equilibrium Blackout (B5)	18
Dynamic Derivative Blackout (B6)	0.02
Dynamic Time Blackout (B7)	20

Note:
To perform an exothermic run, set the Tolerance Parameter (L2) to -1.

See Table 1 for a listing of the factory default settings. A more in-depth explanation of these parameters is found on the corresponding parameter group help pages. These default settings remain in effect until changed by the user. Should the user ever wish to return to the factory default settings, go to the Program Info and Control Menu, User/Factory Settings, touch Reload Factory Default Settings and YES. Non-volatile memory is provided to retain any and all operator initiated program changes; even if power is interrupted or the unit is turned off. If the unit experiences an intentional or unintentional "Cold Restart", the controller will return to the last known settings.

The default parameters of the 6772 Calorimetric Thermometer can be changed to guarantee that the thermometer, when cold restarted, will always be in the desired configuration before beginning a series of tests. Users who wish to permanently revise their default settings may do so using the following procedure:

- Establish the operating parameters to be stored as the user default settings.
- Go to the Program Info and Control Menu, User/ Factory Settings, User Setup ID, and enter the desired User Setup ID.
- Select Save User Default Settings

To re-load the user default setting, go to the Program Info and Control Page, User/Factory Settings, Re-load User Default Settings, and YES.

Performing an analysis
Tests can be run in a strictly manual fashion or automatically where the thermometer sequences the calorimeter through the pre and post periods. The manual sequencing approach is useful for applications where raw data is logged and subsequently analyzed, off-line. In the automatic mode, the thermometer fully sequences the test and applies real time corrections to the calorimeter temperature rise in order to correct for all systemic heat leak effects. In either case, the operator must determine the appropriate temperature source for the jacket.

- Probe – This method uses a thermistor probe attached to the jacket wall to measure the actual temperature of the surroundings (at the chosen point) and the heat leak correction are based upon the actual differences between the bucket and this external jacket temperature.

- Calculated – During the initial equilibrium period this method analyzes the actual heat leak rate and calculates the apparent temperature of the surroundings which would generate this rate and applies this calculated jacket temperature for the determination.

- Fixed – In this method the operator determines what his jacket temperature will be and enters it into the thermometer. All heat leak corrections are then based upon this fixed jacket temperature.

For most applications the calculated method is recommended.

Sample size

The rotating sample cell will hold up to 20 ml of liquid sample or a solid sample weighing up to one gram. More than one gram of solid may be used in some cases, but smaller samples are preferred so that the heat capacity and ionic strength of the system will not change significantly when the reactants are mixed. The Dewar must be filled with not less than 90 ml and not more than 120 ml of liquid to properly cover the rotating cell.

Filling the Dewar

It is best to lift the Dewar out of the air can during the filling operation. The liquid to be placed in it can be measured volumetrically, or the Dewar can be placed on a solution or trip balance and filled by weight. After filling the Dewar, set it in the air can and gently push the spacer ring down as far as it will go.

Loading a solid sample

Solid samples should be suitably ground so that they will dissolve quickly or mix uniformly with the liquid in the Dewar. Place the 126C PTFE Dish on an analytical balance and weigh the sample directly into the dish. Be careful not to drop any of the sample into the push rod socket. After the final weighing, set the dish on a flat surface and carefully press the glass bell over the dish to assemble the cell. Do not grasp or press the thin-walled glass stem during this operation; it is fragile and will break easily. Instead, grasp the bell and press it firmly onto the dish. Then lift the cover from the calorimeter and attach the cell to the stirring shaft by sliding the plastic coupling onto the shaft as far as it will go and turning the thumbscrew finger tight. If the thumbscrew is not tight against the shaft, the contents will not be released. If necessary, use a 9/64 Allen wrench to tighten further. Hold the cover in a horizontal position and lower it carefully until the bottom of the rotating cell rests on a firm, flat surface; then insert the push rod through the pulley hub and press the end of the rod into the socket in the 126C Sample Dish.

Loading a liquid sample

Liquid samples can be measured into the rotating cell either by volume or by weight. Best precision is obtained by weighing, but filling from a volumetric pipette may be adequate in some cases. Set the 126C PTFE Dish on a flat surface and press the glass bell over the dish, handling the glass carefully as described above. If the sample is to be weighed, tare the empty cell on a laboratory balance; insert a pipette through the glass stem and add the liquid, then reweigh the cell. Attach the cell to the stirring shaft and insert the push rod.

Installing the loaded cover assembly

Install the thermistor probe in the cover opening and press the bushing firmly into place to anchor the probe in its proper position. Lower the cover assembly with the cell and thermistor probe into the Dewar and set the cover in place on the air can, then drop the drive belt over the pulleys and start the motor as required.

Combining the reactants

Each test in a solution calorimeter can be divided into three distinct time periods:

1. A pre-period during which the reactants are allowed to come to an initial thermal equilibrium. The thermometer will beep to inform the operator that it has established the initial equilibrium and that it is now time to initiate the reaction.

2. A reaction period during which the reactants are combined and an enthalpy change occurs in the system.

3. A post-period during which the calorimeter again comes to equilibrium. The thermometer will produce a report when the final equilibrium has been achieved and that the test is complete.

At the end of the pre-period, start the reaction by pressing the push rod downward to drop the sample out of the rotating cell. This should be done quickly without interrupting the rotation of the rod without undue friction from the finger. Push the rod down as far as it will go; after which it should continue to rotate the pulley. Let the stirrer continue to run during the reaction and the calorimeter reports its results.

Emptying the calorimeter

Stop the calorimeter motor, raise the cover carefully and wipe any excess liquid from the parts that were immersed in the Dewar. Remove the thermistor probe from the cover and remove the sample dish from the end of the push rod; then remove the rod and release the glass cell from the drive shaft. Lift the Dewar out of the air can and empty it; then wash and dry all wetted parts carefully.

The two operating modes, (manual or automatic) are outlined below:

Manual Test Sequencing

Some users may wish to construct their own thermo gram and apply the classic graphical corrections developed by Dickenson and others. In this case, the actual temperatures can be logged to the memory of the thermometer and then analyzed at the end of the test. These logged temperatures can be recalled to display on the thermometer, printed on an attached printer or transferred to a computer using either the Ethernet Connection or a Compact Flash Card. The Ethernet Connection can also be used to transfer temperatures to a computer for plotting.

First, select the appropriate jacket temperature source as described previously. Then fill the Dewar. Next, prepare and load the reaction. After the calorimeter is fully assembled, turn on the motor, and then turn on the stirrer by pressing the stirrer key on the calorimeter operation menu screen. Turn on the data logger (accessed via the Diagnostics page) in order to periodically record the bucket or calorimeter temperature. The bucket temperature is updated every 12 seconds. Turn on the calorimetric pre-period. The pre-period should last for 6-7 minutes. After the 6-7 minute pre-period test phase, start the reaction by pressing the push rod downward to drop the sample out of the rotating cell. This begins the reaction and subsequent post-period. The calorimeter temperature should begin to significantly change at this point, indicating sample reaction. The calorimetric post-period should last for an additional 6-7 minutes from sample introduction. At the conclusion of the post-period, turn the stirrer off by pressing the stirrer key once again. The motor switch may be left in the "on" position for subsequent tests. Empty and clean the calorimeter.

If the data log destination is a log file, the log file is located at /flash/datalog.csv and may be retrieved via FTP. The log file is easily imported into a spreadsheet program where the calorimeter temperature can be plotted in order to realize a thermal curve. Instructions for working with or analyzing thermal curves are found in the calculations section.

Automatic Test Sequencing

The solution calorimeter will perform all calculations for the user. To do this, first select the appropriate jacket temperature source. For most applications, the calculated jacket approach works well. First, select the appropriate jacket temperature source as described previously. Then fill the Dewar. Next, prepare and load the reaction. After the calorimeter is fully assembled, turn on the motor, and then press the START key located on the right hand side of the screen. This will activate the stirrer that gently circulates the water that surrounds the glass cell. The thermometer will prompt for the sample ID number and the mass of the sample in grams. This begins the calorimetric pre-period. After the thermometer determines that adequate temperature equilibrium is realized, the thermometer will prompt the user to start the reaction by pressing the push rod downward to drop the sample out of the rotating cell. This starts the calorimetric post-period. The calorimeter temperature should begin to significantly rise at this point, indicating sample combustion. The calorimetric post-period will last for an additional 6-7 minutes until the calorimeter temperature drift rate sufficiently stabilizes. At the end of the post-period the calorimeter will signal the end of the test and generate a report.

Stop the calorimeter motor, raise the cover carefully and wipe any excess liquid from the parts that were immersed in the Dewar. Remove the thermistor probe from the cover and remove the sample dish from the end of the push rod; then remove the rod and release the glass cell from the drive shaft. Lift the Dewar out of the air can and empty it; then wash and dry all wetted parts carefully.

CALCULATIONS

Standardization

A sample of tris (hydroxymethyl) aminomethane, commonly called TRIS, is furnished with the 6755 Calorimeter to provide a reliable standardizing reagent. TRIS is furnished as a dry powder which can be used directly from the bottle as supplied without further preparation, but undue exposure to air and moisture should be avoided in order to preserve the integrity of the standard.

For standardizing the 6755 Solution Calorimeter, solid TRIS can be dissolved in dilute hydrochloric acid in a controlled reaction for which the amount of heat evolved is well established. In the recommended standardization procedure described below, 0.5 gram of TRIS is dissolved in 100 ml of 0.1 N HCl to evolve 58.738 calories per gram of TRIS AT 25 °C.

1. Tare the Dewar on a solution or trip balance and add exactly 100.00 + .05 grams of 0.100 N HCl.
2. Weigh 0.50 +.01 gram of TRIS into the 126C Teflon Dish on an analytical balance to an accuracy of +.0001 g.
3. Assemble the rotating cell; place it in the calorimeter and start the motor.
4. Let the calorimeter come to equilibrium; then initiate the reaction by depressing the push rod.
5. Analyze the thermogram to determine the net corrected temperature rise, ΔTc. At the conclusion of the test the instrument will report a net corrected temperature rise, ΔTc.
6. Calculate the known energy input by substituting in the equation:

$$QE = m[58.738 + 0.3433(25 - T(0.63R))]$$

where:
QE = the energy input in calories
m = weight of TRIS in grams
T(0.63R) = temperature at point 0.63R on the thermogram

Note:
The term, 0.3433(25 – T(0.63R)), adjusts the heat of reaction to any temperature above or below the 25 °C reference temperature.

Calculate the energy equivalent of the calorimeter and its contents by substituting in the equation:

$$e = \frac{QE}{\Delta T_C}$$

where:
e is expressed in calories per °C.

Determine the energy equivalent of the empty calorimeter by subtracting the heat capacity of the 100 g of 0.1N HCl from *e*, as follows:

$$e' = e - (100.00)(0.99894)$$

where:
e' = energy equivalent of the empty calorimeter in calories per °C.
100.00 = mass of 0.100N HCl in grams
0.99894 = specific heat of 0.1N HCl at 25 °C

Example:

A standardization reaction involving 0.5017 grams of TRIS, and 100.00 grams of 0.100N HCl producing a net corrected temperature rise of ΔT_C = 0.244 °C with 0.63 rise, T(0.63R), at 24.301 °C.

In this reaction the known energy input is:

$$QE = 0.5017\,[58.738 + 0.3433\,(25 - 24.301)]$$
$$= 29.589 \text{ calories}$$

The energy equivalent, *e*, of the calorimeter and its contents is then computed:

$$e = \frac{29.589}{0.244}$$
$$= 121.27\,\frac{cal}{^\circ C}$$

The energy equivalent, *e'*, of the empty calorimeter is then computed:

$$e' = 121.27 - (100)(0.99894)$$
$$= 21.38\,\frac{cal}{^\circ C}$$

Calculating the Energy Change

The energy change, Q, measured in this calorimeter is calculated by multiplying the net corrected temperature change, ΔT_C, by the energy equivalent, e, of the calorimeter and its contents.

$$Q = (\Delta T_C)(e)$$

If ΔT_C is measured in °C and e is expressed in calories per °C, Q will be reported in calories. (The energy equivalent, e, is determined by a standardization procedure).

The change in enthalpy, ΔH, at the mean reaction temperature is equal to -Q divided by the amount of sample used in the experiment, expressed either in moles or grams.

$$\Delta H_T = \frac{-Q}{m}$$

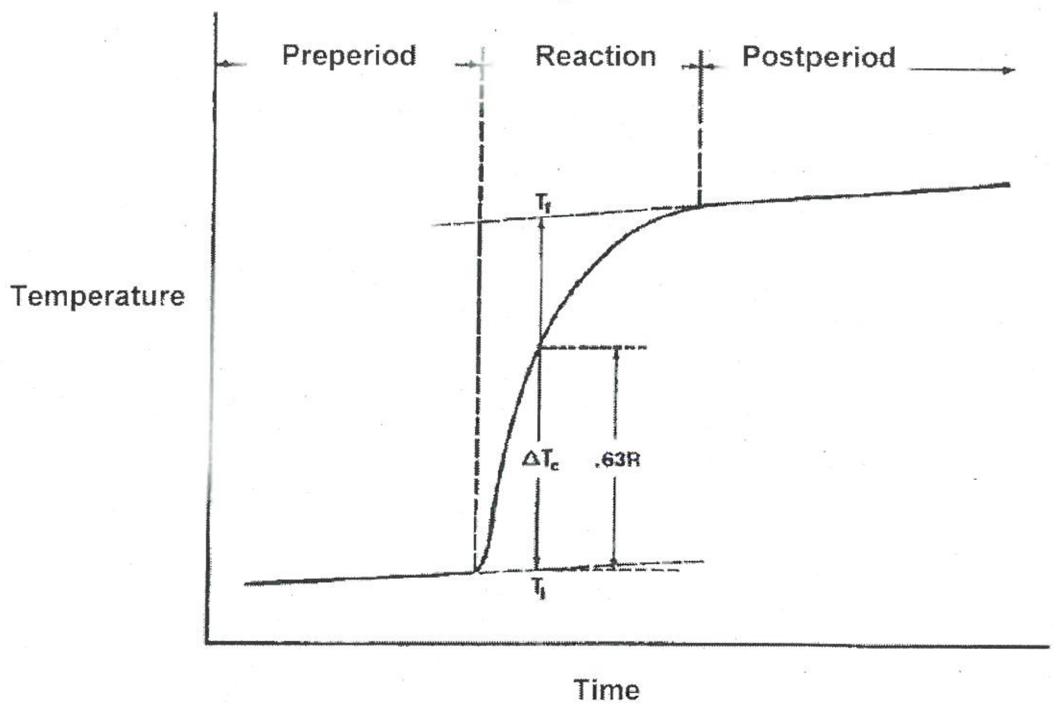
where T is the temperature at the 0.63R point on the thermogram.

Enthalpy values are usually expressed in kilocalories per mole.

Procedures for converting enthalpy changes, ΔH, to thermodynamic standard conditions and for using ΔH in other computations can be obtained from thermodynamics or thermochemistry textbooks, or from literature references.

Reading the Thermogram

Figure 2
Thermogram



In order to determine the net temperature change produced by the reaction, it is necessary to interpolate a point on the thermogram at which the temperature reached 63 percent of its total rise. This can be done easily by following Figure 2, although other variations of this method can be used as well.

1. Place a straight edge over the preperiod drift line and extend this line well past the point at which the reaction was initiated.
2. Move the straight edge to the postperiod drift line and extrapolate this line backward to the firing time. If there are fluctuations in the drift lines due to noise or other variations in the signal, use the best average when drawing these extrapolations.

3. Using a centimeter scale, measure the vertical distance, R, between the two extrapolated lines at a point near the middle of the reaction period.

4. Multiply the distance, R, by 0.63.

5. Set the zero end of the centimeter scale on the extrapolated preperiod drift line and move the scale along this line to locate a vertical intercept with the thermogram which is exactly 0.63R above the preperiod drift line. Draw a vertical line through this point to intercept both drift lines.

6. Read the initial temperature, and the final temperature, at the points of intersection with the drift lines and subtract to determine the corrected temperature rise, ΔT (see Figure 2)

   $\Delta T_c = T_f - T_i$

REPORTS

The 6772 Calorimetric Thermometer can transmit its stored test data in either of two ways. The Auto Report Destination key on the Reporting Controls Menu toggles the report destination between the display and an optional printer connected to the RS232 printer port of the Calorimetric Thermometer. Test results are stored as files using the sample ID number as the file name. A listing of the stored results is accessed by pressing the REPORT command key. The REPORT command key brings up a sub-menu on which the operator specifies.

Select From List This key displays the stored results specified with the following two keys.

Run Data Status This key enables the operator to display five report options:

- only preliminary and final reports
- only final reports
- only preliminary reports
- only pre-weighed sample reports
- all stored reports.

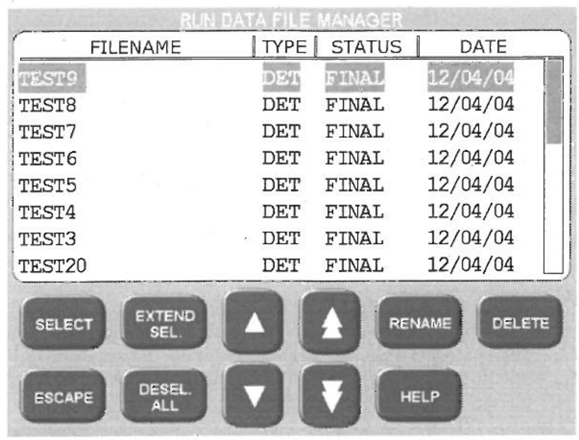
The displayed files can be sorted by filename (sample ID number), by type, by status or by date of test by simply touching the appropriate column. Individual files can be chosen by highlighting them using the up and down arrow keys to move the cursor. Press the SELECT key to actually enter the selection. Once selected the highlight will turn from dark blue to light blue. A series of tests can be selected by scrolling through the list and selecting individual files. The double up and down keys will jump the cursor to the top or bottom of the current display. If a range of tests is to be selected, select the first test in the series, scroll the selection bar to the last test in the series and press EXTEND SEL to select the series.

The DESEL ALL key is used to cancel the current selection of files.
To bring the selected report or series of report to the display, press the DISPLAY key. To send the reports to the printer press the PRINT key.

MEMORY MANAGEMENT

The 6772 Calorimetric Thermometer will hold data for 1000 tests in its memory. These tests may be pre weights, preliminary or final reports for either calibration or determination runs. Once the memory of the controller is filled, the controller will not start a new analysis until the user clears some of the memory.

The FILE MANAGEMENT key on the main menu leads to the file management sub-menu. The RUN DATA FILE MANAGER key leads to a listing of the files. Single files can be deleted by highlighting the file and pressing the DELETE key. The controller will then ask the user to confirm that this file is to be deleted. A series of files can be deleted by selecting the first file in the series and then the last file in the series using the EXTEND SEL key and then pressing the DELETE key.



The controller of the 6772 Calorimetric Thermometer can accept SD memory cards. These cards can be used to:

- Copy test file data for transfer to a computer
- Copy user settings for back up
- Reload user settings to the controller to restore or update the controller's operating system.
- Copy the data log file for transfer to a computer.

SD memory cards are inserted into the slot on the back of the control section of the Calorimetric Thermometer. Keys are provided on the FILE MANAGEMENT sub-menu to initiate some of these functions. The data log is transferred from the User Defined Functions Menu on the Diagnostics Menu.

TROUBLESHOOTING

Error List
The calorimeter will run a number of diagnostic checks upon itself and will advise the operator if it detects any error conditions. Most of these errors and reports will be self-explanatory. The following list contains errors that are not necessarily self-evident and suggestions for correcting the error condition.

A Misfire Condition Has Been Detected. This error will be generated in the event the total temperature change fails to exceed 0.5 °C after the first minute of the post-period. Note that if your reaction is endothermic that you may have to change the L2 parameter to -1. This is found in the Main Menu -> Diagnostics -> Calorimetry Parameter -> Tolerance (L) Parameters.

A Preperiod Timeout Has Occurred. The calorimeter has failed to establish an acceptable initial temperature within the time allowed. Possible causes for this error are listed below:

- A cell leak.
- Poor bucket stirring.
- Lid not tight.
- Initial Dewar temperature outside the acceptable range.

The Current Run Has Aborted Due To Timeout. The calorimeter has failed to establish an acceptable final temperature within the time allowed. Possible causes for this error are listed below:

- A cell leak.
- Poor bucket stirring.

There Is A Problem With The Bucket Thermistor. Possible electrical open or short. This error will result if the temperature probe response is not within the expected range. Probe substitution can be useful in determining the cause of the problem (probe or electronics). The valid working range of the probe resistance is 1000 to 5000 ohms.

- Check connection.
- Replace probe.

There Is A Problem With The Jacket Thermistor. Possible electrical open or short. This errors will result if the temperature probe response is not within the expected range. Probe substitution can be useful in determining the cause of the problem (probe or electronics). The valid working range of the probe resistance is 1000 to 5000 ohms.

- Check connection.
- Replace probe.

You Have Exceeded The Run Data File Limit (1000 Files). The memory set aside for test runs has been filled. Use the memory management techniques to clear out non-current tests.