

SINGLE RUN HEAT CAPACITY MEASUREMENTS

III. Data analysis*

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An outline for the data analysis of single-run heat capacity measurements by dual sample DSC is presented with the following features: 1. Heat flow correction by subtracting the contribution due to the sample pan, including correction for mismatched pan masses. 2. Heat flow and temperature correction with a nonlinear temperature calibration, temperature lag correction, and heating rate correction. 3. Calculation of the cell constants for both cell positions and evaluation of the asymmetry factor between cell positions A and B. 4. Heat capacity calibration and calculation with slope and asymmetry correction. 5. Calculation of heat capacity for multiple runs. 6. Data curve fitting for heat capacity.

Keywords: heat capacity, data analysis, differential scanning calorimeter, DSC, single run

Introduction

In the previous papers of this series [1, 2] the feasibility of single run heat capacity measurements above room temperature and at subambient temperature were proven. These measurements were based on a prior mathematical analysis of the approach [3]. The equipment used for the study was the dual sample differen-

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(DSDSC) with an Autosampler manufactured by TA Instruments, Inc. The details of the instruments and experiments were described previously [1, 2]. For the heat capacity, data were analyzed by newly developed software written in Microsoft® QuickBASIC version 4.0 (registered trademark of the Microsoft Corporation). We found that the major errors in the measurement were caused by environmental fluctuations above room temperature and by the low temperature isotherms at subambient temperature. Several other errors could be identified and should be corrected for precision heat capacity data [1–3].

Recently heat capacity software has become commercial available from TA Instruments, Inc. which has the following features [4]:

- Corrects for contributions due to sample pan weight differences.
- Corrects for instrument baseline.
- Calculates the *actual* heating or cooling rate.
- Calculates the calibration constant for each data point using NIST sapphire standard values or an operator-selected reference material.
- Calculates the heat capacity at each temperature.
- Integrates the total heat capacity to obtain total enthalpy.
- Provides for the exclusion of reaction and transition peaks from the calculations.

We have run the program (kindly provided by TA Instruments). The program is well written and easy to use. In routine use, after suitable calibration, it allows to generate heat capacity with only one scan and ten keystrokes. The questions that remain and need to be addressed are:

- The quality of baseline matching between sample and empty runs remains unknown to the operator.
- Several data corrections are not included, such as temperature calibration, temperature lag correction, and the effect of heating rate differences between sample and reference, which have been found in our previous publications to be of importance in high quality heat capacity computation.
- There is a restricted rule on collecting data and one cannot analyze multiple/repeat runs.
- The data analysis is only designed for a single sample DSC (SSDSC), not for the dual sample DSC (DSDSC) which has shown improvement in heat capacity measurements.

The here described software will address all these problems and incorporate most features of the proprietary software. In this paper, a brief description of the single-run heat capacity software for the DSDSC is given. A copy is available from the authors by mailing an empty, formatted 3.5" 2MB diskette. The program is a compiled QuickBASIC® version and runs on IBM compatible computers. Any comment and suggestion on this program is naturally welcome and can help us in future updates.

Software of this type is hoped to help make the thermal analyst aware of the detailed calculations carried out and permit full understanding of the mathematical tools used.

Heat capacity calculation

The heat capacity of a material undergoing a constant heating or cooling rate is proportional to the heat flow at any temperature. The basic equation is:

$$C_p = \frac{60K\Delta HF}{qW} \quad (1)$$

where C_p is the specific heat capacity in J/(K g) at a given temperature, K is the cell constant (a function of temperature) in dimensionless units, ΔHF is the heat flow into the sample at the given temperature in mW , W is mass of the sample in mg, and q is the heating or cooling rate in deg/min and 60 is the converting factor from minutes to seconds.

As discussed earlier [3], the heat capacity from DSC experiments based on heat conduction should be expressed as follows:

$$C_p = (K\Delta T / q) + [(K\Delta T / q) + C_p'] (d\Delta T / dT_s) \quad (2)$$

where ΔT is the temperature difference between reference and sample (directly accessible from DSC recording), T_s is the sample temperature, K is a temperature-dependent constant, determined by a calibration standard like sapphire (Al_2O_3) [5], q is the heating rate and C_p' is the heat capacity of the empty aluminum pan. The second term in Eq. (2) is small and not directly recorded in standard DSC. It corrects for the difference in heating rate between reference and sample. To get precise heat capacity data, one should consider this small term which may cause an error of about 0.3%, as was discussed before [1]. Since ΔT is proportional to the heat flow [2], $d\Delta T/dT_s$ is proportional to the slope of the heat flow vs. temperature curve. Only for a horizontal baseline (slope = 0) is the heat capacity exactly equal to $K\Delta T/q$, which is the implied assumption for Eq. (1). Obviously this is not true for most cases. Even worse, this quantity cannot be evaluated if the slope is altered electronically without recording the change.

To get ΔT from the DSC recording, we have established the correlation between ΔT and heat flow [2]. The heat capacity of the empty aluminum pan, C_p' is the heat capacity of pure aluminum, well represented in the literature [6]. It is thus not difficult to calculate the heat capacity using the full expression of Eq. (2).

For a single run heat capacity measurement with the DSDSC, C_p can be expressed as follows:

$$\frac{C_{pB}}{C_{pA}} = \frac{(K_B\Delta T_B / q) + [(K_B\Delta T_B / q) + C_p'] (d\Delta T_B / dT_B)}{(K_A\Delta T_A / q) + [(K_A\Delta T_A / q) + C_p'] (d\Delta T_A / dT_A)} \quad (3)$$

where all symbols are as in Eq. (2), except for the subscripts A and B which refer to the two sample positions in the DSDSC cell. We can rewrite Eq. (3) to the following:

$$\frac{C_{pB}}{C_{pA}} = \frac{K_B \Delta T_B}{K_A \Delta T_A} \left[\frac{1 + [1 + (qC'_p) / (K_B \Delta T_B)] (d\Delta T_B / dT_B)}{1 + [1 + (qC'_p) / (K_A \Delta T_A)] (d\Delta T_A / dT_A)} \right] \quad (4)$$

which, in the program, is called the heat capacity with full slope correction. On neglecting the ratio $C'_p/C_{pB} \approx C'_p/(K_B \Delta T_B/q)$ and similarly $C'_p/C_{pA} \approx C'_p/(K_A \Delta T_A/q)$, the heat capacity of the empty pan relative to the appropriate total heat capacities $K\Delta T/q$, one gets the simpler expression:

$$\frac{C_{pB}}{C_{pA}} = \frac{K_B \Delta T_B}{K_A \Delta T_A} \left[\frac{1 + (d\Delta T_B / dT_B)}{1 + (d\Delta T_A / dT_A)} \right] \quad (5)$$

which, in the program, is called the heat capacity with partial slope correction. Assuming a horizontal baseline (the slope $\propto d\Delta T/dT = 0$) or the same slope for A and B ($d\Delta T_A/dT_A = d\Delta T_B/dT_B$), we will get the heat capacity without slope correction (with asymmetry correction only):

$$\frac{C_{pB}}{C_{pA}} = \frac{K_B \Delta T_B}{K_A \Delta T_A} = \frac{K_B \Delta HF_B}{K_A \Delta HF_A} \quad (6)$$

which, in the program, is called the heat capacity with asymmetry correction. Here K_B/K_A is the asymmetry factor, discussed before [2]. If the DSDSC cell were symmetric for the two sample positions ($K_A = K_B$), the heat capacity would be calculated simply by the equation:

$$C_{pB} = C_{pA} \frac{\Delta T_B}{\Delta T_A} = C_{pA} \frac{\Delta HF_B}{\Delta HF_A} \quad (7)$$

which is called heat capacity without correction.

By placing a sapphire standard on position A and an unknown sample on position B, one can thus calculate the heat capacity of an unknown sample from the heat flows in a single DSC run. The advantage of the single run experiment is not only the simple computation, but also the ability to compensate internally for overall fluctuation during the experiment as long as sample and reference are affected equally.

Data corrections

In order to get corrected heat flows due to the actual samples at corrected temperature, several data corrections must be made and a spline function has been used to match

the temperature interval between empty and sample runs before calculating the heat capacity.

Temperature calibration

Although the DSC has a build-in two-point linear temperature calibration option, we found previously [2] that it is not sufficiently linear over a wide temperature range, especially at low temperature. It is better to collect the data without temperature correction, and correct with the data calculation software.

In the software we use a second order polynomial for the temperature calibration:

$$\Delta T_1 = C_0 + C_1T + C_2T^2 \quad (8)$$

where ΔT_1 is the temperature difference between corrected and observed values, T is temperature of the standard material in K, C_0 , C_1 , and C_2 are the parameters for the temperature calibration.

The standard samples for transitions used in our laboratory are cyclohexane ($T_d = 186.1$ K, $T_m = 279.7$ K), cycloheptane ($T_d = 134.8$ K, $T_m = 265.1$ K), cyclooctane ($T_d = 166.5$ K, $T_m = 288.0$ K), 1-chlorobutane ($T_m = 150.1$ K), 2-chlorobutane ($T_m = 141.9$ K), *n*-octane ($T_m = 216.4$ K), naphthalene ($T_m = 353.4$ K), indium ($T_m = 429.8$ K), tin ($T_m = 505.1$ K), KNO_3 ($T_m = 607$ K), etc. Eq. (8) can be fitted with up to 9 transition data. If only two transitions are available, Eq. (8) will reduce to a linear equation, *i.e.* $C_2 = 0$.

Temperature lag from the amplitude of heat flow

The temperature lag of the amplitude of the heat flow can be corrected by determining linear slope of the onset of the sharp phase transition of the standard samples:

$$\Phi = \frac{dHF}{dT} \quad (9)$$

These slopes (Φ) depend on the DSC cell of the instrument, the type of sample pan, the sample material and the temperature (details to be published later). Under the same experimental conditions, the onset slope might show some temperature dependence. Here we also introduce a second order polynomial equation:

$$\Phi = B_0 + B_1T + B_2T^2 \quad (10)$$

and the temperature lag from the amplitude of the heat flow can be expressed as follows:

$$\Delta T_2 = \Delta HF / \Phi = \Delta HF / (B_0 + B_1T + B_2T^2) \quad (11)$$

Temperature lag correction as a function of heating rate

As illustrated in previous experiments [1, 2], the transition temperature of standard samples changes linearly with the heating rate because of the temperature lag, *i.e.*

$$\Delta T_3 = Dq \quad (12)$$

where q is heating rate in deg/min, D is a constant depending on the type of pan. typical values for D are 0.025 for a non-hermetically sealed aluminum pan and 0.075 for a hermetically sealed aluminum pan.

The original recorded temperature should thus be corrected as follows:

$$T_{\text{correct}} = T_{\text{recorded}} - \Delta T_1 - \Delta T_2 - \Delta T_3 \quad (13)$$

The parameters $C_0, C_1, C_2, B_0, B_1, B_3$ of Eqs. (8) and (11) can be updated from new temperature calibration results on standard samples or changed from one file to another as is desired in the software.

Heat flow correction from the changes in the heating rate

Usually, heat capacity measurements are made at a constant heating rate. The actual heating rate, however, might deviate from the preset value, especially at the beginning of linear heating and in the vicinity of transitions regions. From Eq. (1), one can see that the heat flow is proportional to the heating rate, thus, the heat flow must be corrected to the preset value as follows:

$$\Delta HF_0 = \Delta HF (q_0 / q) \quad (14)$$

where ΔHF_0 is the corrected heat flow, q_0 is the preset (expected) heating rate, and ΔHF and q are the actually recorded heat flow and heating rate, respectively.

Heat flow correction from the difference of pan mass

For heat capacity measurement, it was found best to have aluminum pans of the same or similar masses [7]. Even though it seems trivial to correct for the heat capacity difference, it has been our experience that runs with minimal correction of mass differential are more precise. For the minor correction, after matching pans as best as possible, one can subtract the heat flow due to the mismatched pan masses based on the heat capacity of aluminum, *i.e.*

$$\Delta HF_0 = \Delta HF + \frac{C_p^{\text{Al}} q \Delta W}{60K} \quad (15)$$

where ΔHF_0 and ΔHF are the corrected and recorded heat flows, respectively. C_p^{Al} is the heat capacity of aluminum, q , the heating rate, K , the cell constant, ΔW , the mass difference between the empty pan and the sample pan.

In our earlier instrument evaluation of the effect of the change of pan mass on the change of heat flow. The calculated heat capacity of aluminum pan from the slope of the change of baseline was found to be proportional to the change of baseline vs. the change of aluminum pan mass was, however, 1/3 lower than expected. Usually, all pan weights are recommended to be adjusted to within ± 0.1 mg when no correction is to be made for the difference of pan mass. Even with a correction, the mismatch should be limited to ± 0.3 mg since an equivalent ± 0.1 mg error might be introduced by correcting with the calculated heat capacity (which at least in one of our tests was 1/3 lower than expected).

Data requirements

Data collection

A. The mass of pans and sample need to be established with a microbalance with an accuracy of better than $\pm 0.05\%$. The pan material and type must be the same for all data. For heat capacity measurements the sample mass should be as large as possible for the given pan type. Experience has shown 10–30 mg to be suitable for macromolecules. The pan masses should be matched as well as possible. If there is a mismatch between pan masses, a correction must be made when calculating the heat capacity. Normally, this mismatch should not be over ± 0.5 mg. It is naturally required to reweigh the sample after each run to check for losses that could occur due to moisture loss or decomposition.

B. All samples should be placed by the Autosampler to minimize effects due to variation in sample position [1].

C. Set the method parameters as indicated:

- 1) Set sampling interval.
- 2) Equilibrate at a temperature 10–20 K below the temperature region of interest.
- 3) Hold at this temperature isothermally for at least 3 minutes to equilibrate. (If a steady state with constant heat flow cannot be achieved, correct the instrument performance. A stable isotherm governs much of the final data quality.)
- 4) Measure at a heating rate of 5–20 deg/min to maximum temperature of interest range. (Higher heating rates show excessive lags, lower heating rates decrease the heat flow to affect precision).
- 5) Hold isothermal from, again, at least 3 minutes to equilibrate. (The same comment applies as to point 3. If either isotherm is unsteady, the run must be discarded.)
- 6) If there is to be more than 1 run, repeat the procedure starting at 2. (Note that for quality measurement at least 3 measurements should be made, preferably on different samples.)

7) If you run the sample below room temperature, a cooling accessory must be attached. (Our experience with low temperature measurements have been discussed in Ref. 2.)

Here is a typical method sequence from our laboratory, as set up with the TA Instruments software:

1. Sample interval 3.0 seconds/point
2. [Event on]
3. Equilibrate at -100°C
4. [Data storage on]
5. Isothermal for 30 minutes
6. Ramp $10^{\circ}\text{C}/\text{min}$ to 100°C
7. Isothermal for 5 minutes
8. [Data storage off]
9. [Event off]
10. [Repeat segment 2 for 3 times]

The segments in bracket are optional for low temperature and/or repeating runs.

D. Start to run experiment by using above method.

E. Repeat above procedure for others (empty pan, sapphire standard or unknown samples) at the same temperature range.

Note that heat capacity can only be measured accurately over a temperature range which shows a linear change in isothermal baseline. In a well adjusted calorimeter this may be 100 K, but is rarely more than 200 K!

Data transfer and conversion

Before using our heat capacity calculation program, the original data file must be transferred from the TA system to MS-DOS by using TAGET command and then convert the (binary) data file to an ASC II data file by using the TACONVRT command. The TAGET and TACONVRT software is included in the User Programmability package of TA instruments. After this conversion the data file has the following structure:

Source binary TA data file: SAPPHIRE.001

15 lines in the parameter block

3 channels of data

Run 1167

Module DSC Dual Sample - Sample A

Sample SAPPHIRE

Size 62.3810 mg

Method -150 to 30°C @ 10 deg/min

Operator JIN

Comment HEAT CAPACITY OF SAPPHIRE STANDARD

Nsig 3
Sig1 Time (min)
Sig2 Temperature (°C)
Sig3 Heat Flow (mW)
Kcell 1.0000
Calib 0.00
Data 26-Sep-91
Time 13:52

0.087 -153.836 -3.89323E-02
0.237 -153.924 -0.03769E-02

The first 20 lines are all information for this file. Starting from line 21, there are three columns data (time, temperature and heat flow respectively). For a multiple runs, the data will be separated by an extra line: -1, -1, -1. The here described data analysis can be applied to any other DSC producing a similar data file.

General performance and examples

When the instrument is well adjusted by hardware calibration, the data corrections in Eqs (13)–(15) for temperature calibration, temperature lag, heating rate and pan mass corrections will be relatively small compared to the heat capacity corrections in Eqs (4)–(6). Here is an example for the heat capacity of aluminum for which details have been shown in the previous paper of this series [2]. The average and RMS errors between experimental and standard data from 180–370 K are $-6.45 \pm 3.29\%$ without correction [(Eq. (7)), $-1.17 \pm 5.57\%$ with asymmetry correction [Eq. (6)], $-1.22 \pm 2.21\%$ with partial slope correction [Eq. (5)] and $-0.77 \pm 2.09\%$ with full slope correction [Eq. (4)].

We have used the here described software to analyze up to the present more than 200 heat capacity runs in the temperature range of 130–600 K. The results are in the process of being published. The various samples were sapphire [2], selenium [2], aluminum [2], quartz [2], polystyrene [2], sodium chloride [2], *n*-paraffins [8], polysilylene [9], N,N'-bis (4-*n*-octyloxybenzal) -1,4- phenylenediamine [10], polysulfones [11], fluorinated *n*-paraffins [12], polyethylene terephthalate fibers [13], nylon 4,6 [14], bisphenol [15], polypivalolactone [16], tetra-*n*-alkylammonium halides [17], polyethers [18], fullerene (C₆₀) [19], etc. All data have been collected in our Advanced THERMAL Analysis System (ATHAS) data bank which includes all published critically evaluated experimental heat capacities, as well as calculated heat capacities of now nearly 200 linear macromolecules and related small molecules [20]. The agreement between experimental and calculated data is usually better than $\pm 3\%$.

More detailed information on operation of the program is listed in the Appendix. Of course, a completed manual will come with the software to anyone who is interested to use it.

* * *

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Zusammenfassung — Es werden die Grundzüge für die Datenanalyse von Wärmekapazitätsmessungen durch Doppelproben-DSC mit Einfachdurchgängen beschrieben:

1. Korrektur des Wärmeflusses durch Subtraktion des Beitrages des Probenbehälters, einschließlich der Korrektur nicht angeglicher Behältermassen. 2. Korrektur des Wärme flus-

ses und der Temperatur mit einer nichtlinearen Temperaturkalibrierung, Korrektur von Temperaturverzögerung und Aufheizgeschwindigkeit. 3. Berechnung der Zellen-konstanten für beide Zellenpositionen und Ermittlung des Asymmetriefaktors zwischen den Zellenpositionen A und B. 4. Kalibrierung der Wärmekapazität und Berechnung mit Anstiegs- und Asymmetriekorrektion. 5. Berechnung der Wärmekapazität für Mehrfachdurchgänge. 6. Kurvenanpassung für die Wärmekapazität.

Appendix

Hardware requirements and installation procedures

The heat capacity calculation program needs a IBM PC, AT, PS/2 and compatibles with at least 250 K of RAM, a hard disk drive and an Enhanced Graphic Adaptor (EGA), or Video Graphic Adaptor (VGA) board for a high resolution monochrome/color monitor. The instrument used to come with a IBM PS/2 Model 60 computer which is sufficient to run this program.

The original program which has been compiled to an executable file is written in QuickBASIC (version 4.0). To install the program and related files, you can use our installation program in the floppy disk. Just insert the disk into the disk drive and type a: or b: to change to that disk drive. Then type CPINSTAL and press Enter (or Return). It will automatic create all the necessary directories and copy all files to the corresponding directory.

Main features

1. Heat flow correction by subtracting the contribution due to the sample pan including the correction for mismatched pan masses. (empty, standard and unknown sample pans)

2. Heat flow and temperature correction with options:

- a. Non-linear temperature calibration from transitions of standards.
- b. Temperature lag correction from heating rate and amplitude of heat flow.
- c. Heat flow correction from deviation of heating rate.

3. Calculation cell constant for both cell positions at each point from sapphire standard data and asymmetry factor between cell positions A and B from the cell constants.

4. Heat capacity calibration and calculation with options:

- a. Slope correction from heating rate differences between sample and reference.
- b. Asymmetry correction for heat capacity calculation.

5. Data output with options:

- a. Device selection among screen, printer and hard disk.

- b. Data interval selection among all data, 1K, *ATHAS* table or specific interval.
6. Heat capacity data fitting with options:
 - a. Linear or polynomial fitting.
 - b. Discarding transition(s) within fitting range.
 - c. Selecting any range for fitting.
7. Others:
 - a. Calculating heat capacity for multiple runs even starting time mismatched.
 - b. Data smooth and rescale plot.

Program operation

Before running the program, all data files which have been converted to ASC II data files must be moved or copied to directory C:\CP\DATA.

To run the program, simply type CP and press Return (or Enter). The batch file CP.BAT will automatically load and run the program. The entire program is function-key driven and relatively simple to operate. Each function key has a brief description on the last three lines of monitor screen. A particular option can be selected by either press function key at desired choice or ESC key to move backward through the program if they are active. You can also exit the program anytime by pressing Ctrl and End simultaneously.

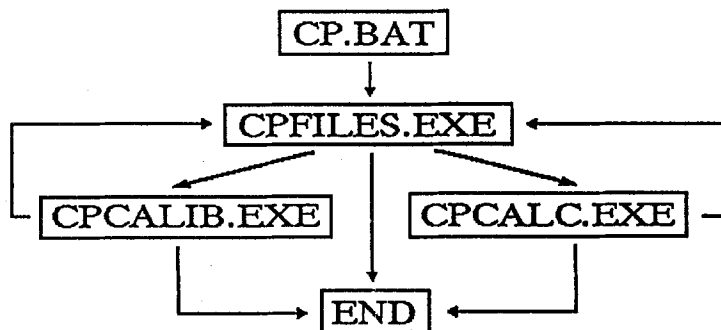
In order to have more memory to hold more data sets, the program has been divided into three main parts which can be chained to each other. The three main parts are:

CFILES.EXE for loading data, matching curves and correcting data.

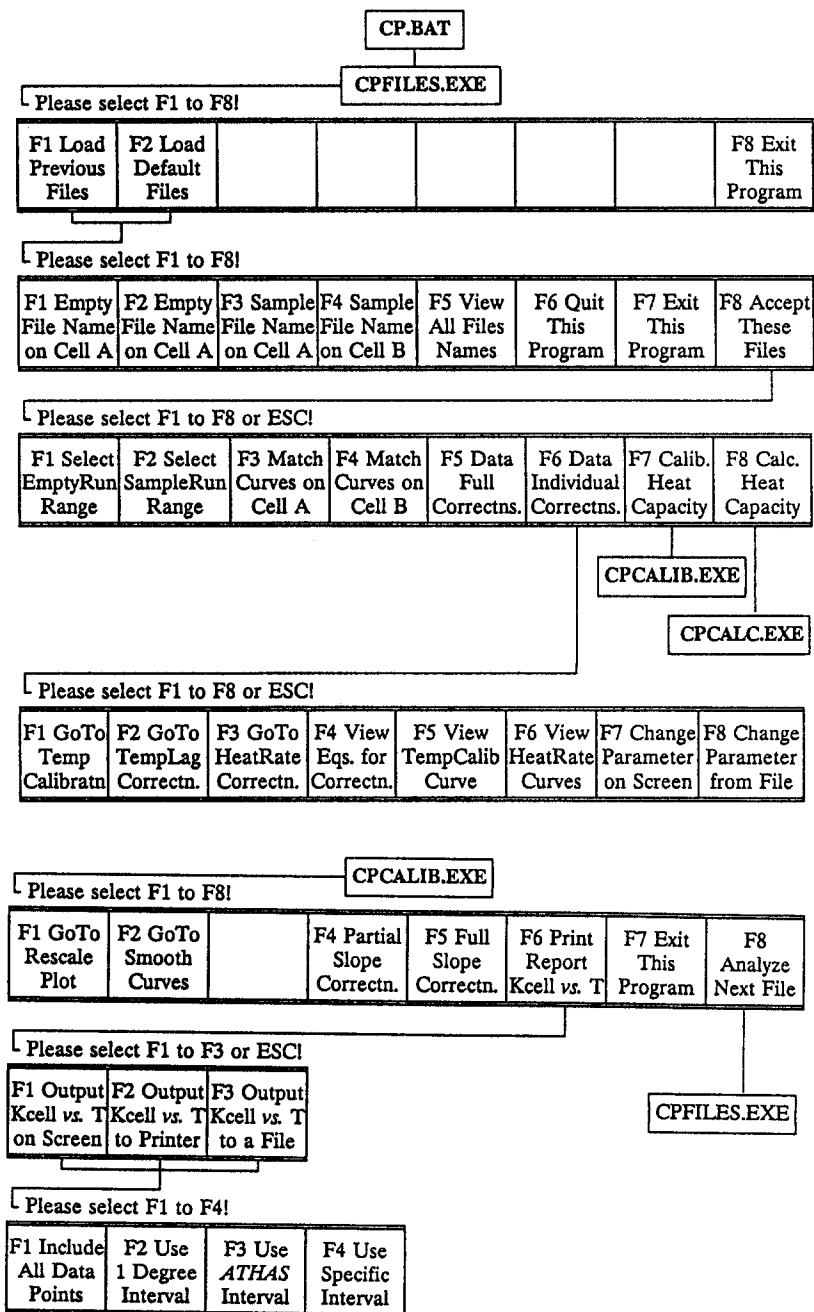
CPCALIB.EXE for calibrating heat capacity between cell positions A and B.

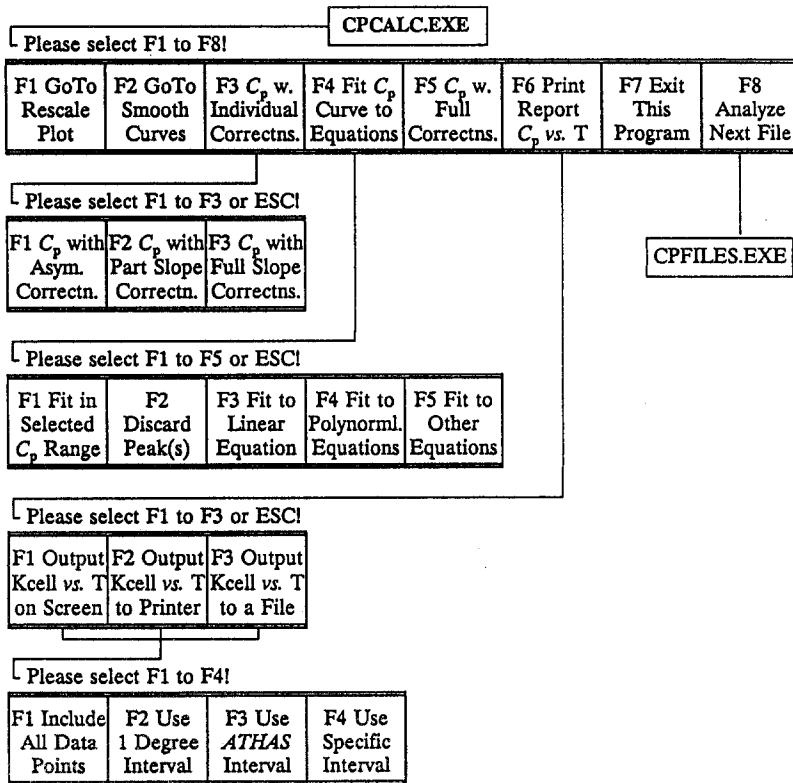
CPCALC.EXE for calculating heat capacity with all correction options.

The main flow chart can be show as follow:



The function key flow chart is as follow:





The detail function key outline

1st menu of CPFILES.EXE:

- F1: Load file names which are used last time.
- F2: Load file names which are used for demonstrating this program.
- F8: Stop the program.

2nd menu of CPFILES.EXE:

- F1: Enter the file name of empty pan on cell A.
- F2: Enter the file name of empty pan on cell B.
- F3: Enter the file name of sample pan on cell A.
- F4: Enter the file name of sample pan on cell B.
- F5: View all four file names.
- F6: Stop this program immediately.
- F7: Save these file names and then stop this program.
- F8: Accept these file names and go to the next menu.

3rd menu of CPFILES.EXE:

- F1: Select a particular empty run from multiple runs.
- F2: Select a particular sample run from multiple runs.
- F3: Match the isotherms between empty and sample runs on cell A to subtract the contribution due to the sample pan.
- F4: Match the isotherms between empty and sample runs on cell B to subtract the contribution due to the sample pan.
- F5: Correct data with temperature calibration, temperature lag correction and heating rate correction together.
- F6: Correct data individually and view or change correction parameters.
- F7: Calibrate heat capacity with two standard sapphire samples to establish asymmetry factor for DSDSC.
- F8: Calculate heat capacity for an unknown sample.

4th menu of CPFILES.EXE:

- F1: Calibrate temperature from transitions of standard samples by using non-linear equation.
- F2: Correct temperature lag from heating rate and amplitude of heat flow.
- F3: Correct heat flow from deviation of heating rate.
- F4: View the equations used for data corrections.
- F5: View the temperature calibration curve from the standard samples.
- F6: View the *actual* heating rate for cells A and B.
- F7: Change or view the parameters of temperature correction on the screen.
- F8: Change the parameters of temperature correction from a file.

1st menu of CPCALIB.EXE:

- F1: Set axis scaling parameters (start, stop, and intervals) to rescale the plot.
- F2: Smooth curves with a smoothing interval you specified.
- F4: Correct data based on Eq. (5).
- F5: Correct data based on Eq. (4).
- F6: Output data results.
- F7: Save the file names and then stop this program.
- F8: Go to 1st menu of CPFILES.EXE for a new file.

2nd menu of CPCALIB.EXE:

- F1: show data results of Kcell vs. T on the screen only.
- F2: Print data results of Kcell vs. T on the printer.
- F3: Write data results of Kcell vs. T in a disk file, which is stored in hard disk.

3rd menu of CPCALIB.EXE:

- F1: Output data results with all data point.
- F2: Output data results with 1 degree interval.
- F3: Output data results with our *ATHAS* standard interval.
- F4: Output data results with specific range and interval.

1st menu of CPCALC.EXE:

- F1: Set axis scaling parameters (start, stop and intervals) to rescale the plot.
- F2: Smooth a curve with a smoothing interval you specified.
- F3: Correct heat capacity individually.
- F4: Fit a curve to equation(s).
- F5: Correct heat capacity with asymmetry and full slope corrections.
- F6: Output data results of C_p vs. T .
- F7: Save the file names and then stop this program.
- F8: Go to 1st menu of CPFILES.EXE for a new file.

2nd menu of CPCALC.EXE:

- F1: Correct heat capacity with asymmetry factor based on Eq. (6).
- F2: Correct heat capacity with partial slope correction based on Eq. (5).
- F3: Correct heat capacity with full slope correction based on Eq. (4).

3rd menu of CPCALC.EXE:

- F1: Select data range for fitting.
- F2: Discard transition peak(s) before fitting.
- F3: Fit data to a linear equation ($C_p = A_0 + A_1T$).
- F4: Fit data to a polynomial equation ($C_p = \sum_{i=0}^n A_i T^i$ where n can be up to 5).
- F5: Fit data to other equations.

4th menu of CPCALC.EXE:

- F1: Show data results of C_p vs. T on the screen only.
- F2: Print data results of C_p vs. T on the printer.
- F3: Write data results of C_p vs. T in a disk file, which is stored in hard disk.

5th menu of CPCALC.EXE:

- F1: Output data results with all data point.
- F2: Output data results with 1 degree interval.
- F3: Output data results with our *ATHAS* standard interval.
- F4: Output data results with specific range and interval.