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1997

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Error analysis of the SORP4 sorption microcalorimeter

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Error analysis of the SORP4 sorption microcalorimeter

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October, 20 1997

1 Introduction

It is rather difficult to intuitively estimate the influence of different types of errors on measurements with the SORP4 and our other sorption microcalorimeters. Therefore I have made computer simulations of SORP4 measurements with different types of errors. This report gives the result of these simulations. The sorption microcalorimetric instruments and the method has been described by Wadsö and Wadsö (1996, 1997).

We have a measurement from which we would like to evaluate the true sample properties. These properties are totally independent of our way of measuring them. From our measurement we get results that may contain measurement errors. When we evaluate the measurements we may have got coefficients etc. wrong, so we make evaluation errors. In this report I assess the influence of these two types of errors on the result from SORP measurements.

2 Analytical treatment

The following nomenclature is used:
The following sign conventions are used here: the parameters marked with a star (*) are always equal to or greater than zero, and the parameter marked with a dagger (†) is usually less than zero ($\Delta_v h$ is the enthalpy of the transition from liquid to vapor, and $\Delta_s h$ is the enthalpy of transition from liquid to sorbed phase, cf. Eq. 3).

If we neglect certain small corrections ('initial' and 'sorption time-lag') and assume that we have a dry sample at the start of the measurement the following equations are used for evaluating SORP measurements:

$$a = 1 - \frac{P_v}{P_{\text{max}}}$$  \hspace{1cm} (1)

$$c = \frac{1}{M \cdot \Delta_v h} \int_0^t P_v(\tau) d\tau$$  \hspace{1cm} (2)

$$\Delta_s h = \Delta_v h \cdot (1 - \frac{P_s}{P_v})$$  \hspace{1cm} (3)

Note that we here work with $a$, $c$ and $\Delta_s h$ as functions of time; not functions of each other.
Equation 1 may be written as follows when an error is added to the thermal power of vaporization:

$$a + e_a = 1 - \frac{P_v + e_{P_v}}{P_{\text{max}}}$$

(4)

This results in the following expression for the error in the activity:

$$e_a = \frac{e_{P_v}}{P_{\text{max}}}$$

(5)

This error at time $t$ is only dependant on the values of $e_{P_v}$ at time $t$.

Equation 2 may be written as follows when an error is added to the thermal power of vaporization:

$$c + e_c = \frac{1}{M \cdot \Delta_v h} \int_0^t (P_v(\tau) + e_{P_v(\tau)}) \, d\tau$$

(6)

The resulting expression for the vapor content error is:

$$e_c = \frac{1}{M \cdot \Delta_v h} \int_0^t e_{P_v(\tau)} \, d\tau$$

(7)

The error is dependent on the whole error-history from the start of the measurement. Errors that change sign (e.g. noise) may cancel out themselves.

Equation 3 may be written as follows when errors are added:

$$\Delta_s h + e_{\Delta_s h} = \Delta_v h(1 - \frac{P_s + e_{P_s}}{P_v + e_{P_v}})$$

(8)

By expanding, using Eq. 3 and neglecting an $e^2$-term we get:

$$e_{\Delta_s h} \approx \frac{e_{P_v}(\Delta_v h - \Delta_s h) - e_{P_s} \Delta_v h}{P_v}$$

(9)

It is interesting to note that $e_{\Delta_s h}$ is inversely proportional to $P_v$, but not dependent on $P_s$.

3 The material data used in the simulations

Table 1 gives the data used for all computer simulations. The output interval of 5 s is used in our normal SORP4 measurements and the other values are also within the ranges commonly used in measurements with SORP4. I have used data for three different types of isotherms: 'linear' (an ideal case), 'sigmoid' (e.g. wood) and 'hydrate' (a stepwise salt hydrate isotherm). Table 2 and Figs 2, 3 and 4 show these three cases.
Table 1: The data used in all simulations.

<table>
<thead>
<tr>
<th>Sample Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample density ($\rho$)</td>
<td>0.2 g/cm$^3$</td>
</tr>
<tr>
<td>Sample height ($h$)</td>
<td>2 mm</td>
</tr>
<tr>
<td>Sample weight ($M$)</td>
<td>52 mg</td>
</tr>
<tr>
<td>Diffusivity ratio ($\delta$)</td>
<td>0.5</td>
</tr>
<tr>
<td>Simulation cells in sample ($n$)</td>
<td>5</td>
</tr>
<tr>
<td>Length of simulation</td>
<td>48 h</td>
</tr>
<tr>
<td>Output interval</td>
<td>5 s</td>
</tr>
</tbody>
</table>

\(^1\delta\) is the ratio of the diffusion coefficients for the sample and for air, respectively.

4 The computer programs

The following MATLAB 4 computer programs were used in the present study (the program codes are given in Appendix B):

**s4s.m** simulates measurements with SORP4. Input are the sample properties; output are the thermal powers, the vapor activity and the vapor content (all as functions of time).

**evalsc.m; evalscf.m** calculate sorption isotherms and heats of sorption from the measured (or simulated) thermal power vectors (the program ending with 'f' is a function used in the present work; evalsc is the normal program).

**master4e.m** contain data needed in the evaluation (a special version of the normally used master4).

**errxx.m** is a program that compares evaluated curves from input data with and without errors (xx is the number of the error simulation).

**inps4s.m** inputs the data files.

**errplot.m** plots the differences between the output from evaluations with and without added errors.
Table 2: The knick-points of the sorption isotherms and sorption enthalpies used in the present paper. The vapor content is in units of g/g and the sorption enthalpy has units of J/g.

<table>
<thead>
<tr>
<th>Linear</th>
<th>Sigmoid</th>
<th>Hydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$c$</td>
<td>$\Delta u h$</td>
</tr>
<tr>
<td>0.00</td>
<td>0.0</td>
<td>-1000</td>
</tr>
<tr>
<td>1.00</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1 shows in what order the programs run.

5 The calculations

Table 3 gives an overview of all error calculations made. The procedures are described in the following sections. The result is given in a large number of figures in Appendix A. To find the result of a certain calculation, look for the err-labels (these are actually the names of the MATLAB m-files generating the results).

NOTE 1: All errors introduced (except noise) increase the absolute values of $P_v$ and $P_s$ (in the present paper).

NOTE 2: In Appendix A the error is given as the difference between the evaluated parameters without any error and the evaluated errors with error added. As an example, let $a_{\text{noe}}(t)$ be the activity calculated without any error added to the simulated thermal powers and $a_{\text{err}}(t)$ the activity calculated with an error added. Then the plots give $a_{\text{noe}}(t) - a_{\text{err}}(t)$ as a function of $a_{\text{noe}}(t)$. This means that if the thermal power of vaporization is increased by the error the signs of the result will be
Figure 1: The use of the programs in the present study. The program 'err1a' and the data files 'linres' and 'linnoe' are examples of data files (MATLAB mat-files); those for the sigmoid and the hydrate cases are called 'sigres' and 'hydres', and 'signoe' and 'hydnoe', respectively). The circles are data, the rectangles are computer programs, and the rounded rectangles are data files. Three different sets of material data are used: 'true' (the data entered into the simulation), 'noe' (the data evaluated without any error), and 'err' (the data calculated with an error added).
Figure 2: The sorption isotherm and corresponding sorption enthalpy for the hypothetical linear case used in the present study.

Figure 3: The sigmoid isotherm and corresponding sorption enthalpy (data for the wood *Eucalyptus regnans* taken from Chrisensen and Kelsey 1959)
Figure 4: The salt hydrate isotherm and sorption enthalpy (morphine sulphate, taken from our own measurements). Note that the enthalpy plot has vapor content on the x-axis for clarity.

as follows:

\[ a_{\text{noe}} - a_{\text{err}} > 0 \]
\[ c_{\text{noe}} - c_{\text{err}} < 0 \]
\[ \Delta s h_{\text{noe}} - \Delta s h_{\text{err}} < 0 \]

When a positive error acts on the thermal power of sorption the following result will be obtained:

\[ a_{\text{noe}} - a_{\text{err}} = 0 \]
\[ c_{\text{noe}} - c_{\text{err}} = 0 \]
\[ \Delta s h_{\text{noe}} - \Delta s h_{\text{err}} > 0 \]

NOTE 3: Figures 7, 8 and 9 are of the same type as the diagrams in Appendix A, but they give the difference between true values (i.e. the values entered into the simulation shown in Figs. 2, 3 and 4) and the values
Table 3: An overview over the error calculations made. The different calculations are in this report called 'errxy', where x is the number to the left and y is the letter in the table head.

<table>
<thead>
<tr>
<th>#</th>
<th>error</th>
<th>T/B†</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>short term noise</td>
<td>T+B*</td>
<td>0.1</td>
<td>0.5</td>
<td>mea.</td>
<td>μW</td>
</tr>
<tr>
<td>2</td>
<td>disturbance</td>
<td>B</td>
<td>20</td>
<td>20</td>
<td></td>
<td>μW (early/late)</td>
</tr>
<tr>
<td>3</td>
<td>disturbance</td>
<td>T</td>
<td>20</td>
<td>20</td>
<td></td>
<td>μW (early/late)</td>
</tr>
<tr>
<td>4</td>
<td>baseline shift</td>
<td>B</td>
<td>1</td>
<td>-</td>
<td></td>
<td>μW</td>
</tr>
<tr>
<td>5</td>
<td>baseline shift</td>
<td>T</td>
<td>1</td>
<td>-</td>
<td></td>
<td>μW</td>
</tr>
<tr>
<td>6</td>
<td>baseline slope</td>
<td>B</td>
<td>0.1</td>
<td>1</td>
<td></td>
<td>μW/24 h</td>
</tr>
<tr>
<td>7</td>
<td>baseline slope</td>
<td>T</td>
<td>0.1</td>
<td>1</td>
<td></td>
<td>μW/24 h</td>
</tr>
<tr>
<td>8</td>
<td>calibration coefficient</td>
<td>B</td>
<td>-</td>
<td>1</td>
<td>10</td>
<td>% too high</td>
</tr>
<tr>
<td>9</td>
<td>calibration coefficient</td>
<td>T</td>
<td>-</td>
<td>1</td>
<td>10</td>
<td>% too high</td>
</tr>
<tr>
<td>10</td>
<td>P_{max}</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>10</td>
<td>% too high</td>
</tr>
<tr>
<td>11</td>
<td>cross-talk</td>
<td>T&amp;B</td>
<td>0.1</td>
<td>1</td>
<td></td>
<td>% cross-talk</td>
</tr>
</tbody>
</table>

† Top (sorption side) or Bottom (vaporization side)
* Random noise independently added to both T and B

calculated without any added error. For the activity they give plots of \(a(t) - a_{noe}(t)\) as a function of \(a(t)\), where \(a(t)\) are the true values and \(a_{noe}(t)\) are the values evaluated without any added error.

NOTE 4: In the hydrate case the slopes of the isotherm are either near zero (rapid change of activity without much change in vapor content) or very high (increase in vapor content at nearly constant activity). When the latter is the case the vapor content increase will move like a front through the sample. In the simulations in which the sample is divided into five parts, each vertical step on the isotherm will be almost completed for one cell before the next (inner) cell may start to increase its vapor content. As a result of this five small steps or peaks may be seen in some of the hydrate result (cf. Fig. 6, 9, err6a and err8b).

5.1 The case with no error

A set of sample data is entered (called 'true') are entered into the simulation. When the output from the simulation is evaluated without any error added
(called 'noe') we will get a result that differs from the input data. The main reason for this difference is that the sample has a thickness and the parts at different depths of the sample will be at slightly different activities (otherwise there would be no flow into the sample) and the evaluation procedure cannot take this into account.

Figures 5 and 6 gives the 'true' and 'noe' sorption isotherms and heats of sorption. The differences seen in the high slopes of the hydrate isotherm will probably be corrected by the 'sorption time-lag' correction procedure being developed. The spikes seen in the hydrate enthalpies are artefacts from the simulation. Figures 7-9 gives the difference between the 'true' values and the 'noe' (no error) values for the three simulated cases when the assumption is made that the activities are correct. Note that it is the differences that is given on the y-axes. The plot is of the sample type as the main result that is given in Appendix A. Some of the steps and kinks seen in Figs. 8 and 9 are artefacts from the simulation (changes in the slopes of isotherms and enthalpies).

5.2 Short term noise

Figures 10 and 11 show typical short term noise from two good baselines. It is seen that the short term noise is quite low (it may be compared with the maximal thermal power $P_{\text{max}}$ that is 975 $\mu$W for SORP4).

Calculations have been made with normally distributed white noise with a standard deviation of 0.1 $\mu$W (err1a) and 0.5 $\mu$W (err1b). The measured noise from simultaneously measured good baselines (Figs. 10 and 11) were also repeated to generate a more realistic (?) short term noise (err1c).

$^1$Values of $a$, $c$ and $\Delta_a h$ are evaluated from the simulations as functions of time. The true values are just given as $a-c-\Delta_a h$-triplets. If there is a difference between the true and the evaluated isotherms it is not possible to state that this is caused by an $a$-difference or by a $c$-difference. To make a comparison between two sets of data one has to choose one parameter as correct, and in Figs. 7-9 I have here chosen the activity. To get the whole picture one must look at the plots of the sorption isotherms (Fig. 5) and the sorption enthalpies (Fig. 6). In Appendix A I make comparisons between data evaluated with and without added errors. As both these data sets have the same origin (the same simulation) the differences between any of them ($a$, $c$ or $\Delta_a h$) may be plotted against time or (as I have done) against the values of one of the variables (I used $a$ evaluated without added error).
Figure 5: Sorption isotherms for the three cases investigated. Solid lines are the input data for the simulations ('true') and dashed lines are the evaluated result with no error added ('noe').
Figure 6: Differential heats of sorption for the three cases investigated. Solid lines are the input data for the simulations ('true') and dashed lines are the evaluated result with no error added ('noe').
Figure 7: The difference between the true sample data (entered into the simulation) and the evaluated sample data with no error added for the linear case. Note that the differences between the values are given on the three y-axes. The activity is taken as being the same in both cases (cf. footnote on page 10).
Figure 8: The difference between the true sample data (entered into the simulation) and the evaluated sample data with no error added for the sigmoid case. Note that the differences between the values are given on the three y-axes. The activity is taken as being the same in both cases (cf. footnote on page 10).
Figure 9: The difference between the true sample data (entered into the simulation) and the evaluated sample data with no error added for the hydrate case. Note that the differences between the values are given on the three y-axes. The activity is taken as being the same in both cases (cf. footnote on page 10).
Figure 10: An example of a good baseline from the bottom (vaporization) calorimeter in SORP4. This is the baseline used in the erric calculations.

Figure 11: An example of a good baseline from the top (sorption) calorimeter in SORP4. This is the baseline used in the erric calculations.
5.3 Disturbance

The effect of a disturbance was tested by adding a half-period sinusoidal curve to the simulated thermal powers. This disturbance is shown in Fig. 12. A disturbance is characterized by its starting time \( t_1 \), its length \( \Delta t \), half a harmonic period) and its amplitude \( P_2 \). Table 4 gives these parameters for the four calculations made. The disturbances only act on one part (top or bottom) a time.

All the disturbances increase the absolute values of the thermal powers. When a higher thermal power of vaporization is measured for some time this will have three effects:

1. The vapor activity will not be correct during the disturbance (afterwards it will be correct again).

2. To the vapor content will be added a small apparent vapor content increase caused by the integration of the disturbance. This vapor content shift seen in the c-result may be calculated by the following equation:

\[
\Delta c = P_2 \frac{\Delta t}{\pi} \int_{0}^{\pi} \sin(t)dt \frac{1}{M \cdot \Delta_v h}
\]

Here the nomenclature is as follows:

\( \Delta c \) vapor content shift \( g/g \)

\( P_2 \) max thermal power of disturbance \( W \)

\( \Delta t \) time of disturbance \( s \)

\( M \) dry mass of sample \( g \)

\( \Delta_v h \) heat of vaporization \( J/g \)

For \( \text{err2b} \) I calculated \( 6.0 \times 10^{-5} \) and measured \( 6.0 \times 10^{-5} \).

3. The heat of sorption will not be correct during the disturbance, but after the disturbance it will be correct again.

When a higher thermal power of sorption is measured only the evaluated enthalpy of sorption will be affected, and only as long as the disturbance is active.
Figure 12: The sinusoidal disturbance added to the thermal power curves in \textit{err2} and \textit{err3}. The disturbance starts at $t_1$, has a duration of $\Delta t$, and has a maximum of $P_2$.

Table 4: The parameters for the disturbances.

<table>
<thead>
<tr>
<th></th>
<th>B/T</th>
<th>$t_1$ / h</th>
<th>$\Delta t$ / s</th>
<th>$P_2$ / $\mu W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>err2a</td>
<td>B</td>
<td>0.5</td>
<td>600</td>
<td>20</td>
</tr>
<tr>
<td>err2b</td>
<td>B</td>
<td>20</td>
<td>600</td>
<td>20</td>
</tr>
<tr>
<td>err3a</td>
<td>T</td>
<td>0.5</td>
<td>600</td>
<td>20</td>
</tr>
<tr>
<td>err3b</td>
<td>T</td>
<td>20</td>
<td>600</td>
<td>20</td>
</tr>
</tbody>
</table>
5.4 Baseline shift

Baseline shift is the same as an error in the determination of the baseline, i.e. $e_{P_v}$ and $e_{P_s}$ are constant. Equations 5 and 7 may be used without any changes. For $a$ the error at time $t$ is only dependent on the values of $e_{P_v}$ at time $t$. For $c$ the error is dependent on the integral of the errors during the whole measurement. For $\Delta_v h$ the situation is more complex, but Eq. 9 may be rewritten as:

$$e_{\Delta sh} \approx \frac{e_{P_v} \Delta_v h - e_{P_v} \Delta_s h - e_{P_s} \Delta_v h}{P_v} = \frac{1}{P_v} (A - B \cdot \Delta_v h)$$  \hspace{1cm} (11)

Here $A$ and $B$ are constants (because $\Delta_v h$ is constant).

In the SORP sorption microcalorimeter we first determine the baseline with only the dry sample in the calorimetric vessel. To start the measurement we then introduce liquid water into the other part of the vessel. Therefore we use the baseline measured without water to correct the measurement with water. I believe that this procedure is correct, but if the baseline was changed by the introduction of water we would have a baseline shift.

Only one calculation with 1 $\mu W$ shift was made for each of the two parts of the vessel: err4a for the bottom (sorption) and err5a for the top (vaporization). Results from other baseline shift may be found by the use of Eqs. 5, 7 and 9.

5.5 Baseline slope

Baseline slope is the same as baseline drift and its comes from the drift of some part of the instrument (e.g. the electronics). Baseline slopes may be written:

$$e_{P_v} = \sigma_v t$$  \hspace{1cm} (12)

$$e_{P_s} = \sigma_s t$$  \hspace{1cm} (13)

Here $\sigma_s$ and $\sigma_v$ are the slopes (in W/s) of the baselines. Equation 5, 7 and 9 may then be written as follows when the errors are included:

$$e_a(t) = \frac{\sigma_v t}{P_{\text{max}}}$$  \hspace{1cm} (14)

$$e_c(t) = \frac{1}{M \cdot \Delta_v h} \int_0^t \sigma_v \tau d\tau = \frac{\sigma_v t}{2M \cdot \Delta_v h}$$  \hspace{1cm} (15)
\[ e_{\Delta_sh}(t) \approx \frac{\sigma_v \Delta_v h - \sigma_s (\Delta_v h - \Delta_s h)}{P_v} \cdot t \]  \hspace{1cm} (16)

The Thermometric thermostated bath we are using is very stable, but we have sometimes seen quite large slopes in the baselines before the measurements, especially for the top (sorption) calorimeter. The cause of this is not yet known, but we guess that the drifts we see are caused by some process in the sorption vessel (e.g. sorption) or non-matching time-constants in the measurement and reference vessels.

Two calculations were made for each of the two parts of the vessel: err6a and err6b for the bottom (vaporization) and err7a and err7b for the top (sorption). The baseline-slopes are given in Table 3. A baseline slope greater than zero increases the absolute value of a thermal power.

### 5.6 Calibration coefficients

For this case Eqs. 5, 7 and 9 have to be modified as the error is not added to, but multiplied with the thermal powers. This can be done by rewriting the errors into the form previously used by first writing:

\[ P_v + e_{P_v} = \kappa_v P_v \]  \hspace{1cm} (17)
\[ P_s + e_{P_s} = \kappa_s P_s \]  \hspace{1cm} (18)

that gives:

\[ e_{P_v} = (\kappa_v - 1)P_v \]  \hspace{1cm} (19)
\[ e_{P_s} = (\kappa_s - 1)P_s \]  \hspace{1cm} (20)

Equation 5, 7 and 9 may be then written as follows:

\[ e_a(t) = \frac{(\kappa_v - 1)P_v}{P_{\text{max}}} \]  \hspace{1cm} (21)

\[ e_c = \frac{(\kappa_v - 1)}{M \cdot \Delta_v h} \int_0^t P_v(\tau) d\tau \]  \hspace{1cm} (22)

\[ e_{\Delta_sh} \approx \Delta_v h (\kappa_v - 1)P_v - (\Delta_v h - \Delta_s h)(\kappa_v - 1)P_v \]  \hspace{1cm} (23)

The calibration coefficients are determined by electrical calibrations. There are some problems associated with this; mainly the introduction of heat conducting copper wires into the vessel. Two error levels were investigated for each of the two parts of the vessel: 1 and 10%. For each calculation the calibration coefficient is this much higher than it should be. The results are called \text{err8b - err8c} and \text{err9b - err9c}.
5.7 Maximal thermal power ($P_{\text{max}}$)

The maximal thermal power of vaporization ($P_{\text{max}}$) is an important parameter in the evaluation of our measurements. It is a measure of the resistance to vapor diffusion from the vaporizing liquid to the sorbing sample. In theory at least, it may be calculated as:

$$P_{\text{max}} = D_p \cdot p_{\text{sat}} \frac{A}{L} \Delta_v h$$  \hspace{1cm} (24)

Here $D_p$ (g/s/m/Pa) is the diffusion coefficient in air with vapor pressure as potential, $p_{\text{sat}}$ (Pa) is the saturation vapor pressure, $A$ (m$^2$) is the cross sectional area of the tube between the chambers, $L$ (m) is the effective length$^2$ of the diffusion tube, and $\Delta_v h$ (J/g) is the enthalpy of vaporization.

Equation 1 may be written as follows when $P_{\text{max}}$ is modified by an error factor:

$$a + e_\alpha = 1 - \frac{P_v}{\kappa_{P_{\text{max}}} \cdot P_{\text{max}}}$$  \hspace{1cm} (25)

This may be reduced to the following expression for the resulting error:

$$e_\alpha = \frac{P_v}{P_{\text{max}}} (1 - \frac{1}{\kappa_{P_{\text{max}}}})$$

In practice, the maximal thermal power is determined from experiments with water in the vaporization chamber and a drying agent or a saturated salt solution in the sorption chamber. Different methods yield slightly different values. The cause of this is not known. The $P_{\text{max}}$-calculations are done with two error levels: 1 and 10%. For each calculation $P_{\text{max}}$ is this much higher than the true values. The results are called err10b - err10c

5.8 Cross-talk

Our double calorimeter is not perfect; one weakness is that a when a thermal signal is generated in one part of the calorimeter a small fraction of it will be measure in the other calorimeter. We call this cross-talk and it may be formally described as:

$$\hat{P}_v = P_v - \delta_{sv} P_s$$  \hspace{1cm} (26)

$^2$The effective length differs from the true length as it must also take into account the diffusive resistance in the top chamber of the calorimetric vessel.
\[ \dot{P}_s = P_s - \delta v_P P_v \]  

(27)

Here the c-coefficients are positive as the absolute values of both \( P_v \) and \( P_s \) will decrease (the endothermic and exothermic heats will be partly decreased by each other). The heat that goes from the top to the bottom need only be counted as cross-talk in the bottom (and vice-versa); we need not count it as an extra loss of heat from the top as that is taken care of by the normal calibration coefficient.

Equation 5, 7 and 9 may be then written as follows:

\[ e_a = \frac{\delta v_P P_s}{P_{\text{max}}} \]  

(28)

\[ e_c(t) = \frac{-\delta v_P}{M \cdot \Delta v h} \int_0^t P_s(\tau) d\tau \]  

(29)

\[ e_{\Delta sh} \approx \frac{P_s}{P_v} \delta v_P (\Delta v h - \Delta s h) - \delta v_P \Delta v h \]  

(30)

Here symmetric cross-talks of 0.1% and 1% are tested (err11a and err11b). In practice the cross-talk does not seem to be symmetric, but the cross-talk will probably not be much different from the cases tested.

6 Discussion and conclusions

When making these conclusions I have defined the following limits of small allowable errors:

\[ a < 0.005 \text{ Pa/Pa} \]
\[ c < 0.0015 \text{ g/g} \]
\[ |\Delta_s h| < 10 \text{ J/g} \]

Errors less than this are allowable with the SORP4 sorption microcalorimeter.

This report shows that

Short-term noise will only disturb the measurements at the end of the measurements (at vapor activities approaching 1.00). The sorption enthalpy is most critical, but it is not difficult to see when the result starts to get wrong as the noise will start to make the curve funnel-shaped.
Disturbances (of unknown shape, size and time) will of course be impos-
sible to correct for. It is, however, known that almost all SORP4 mea-
surement curves are perfectly smooth (except for the noise), so distur-
bances are rare, and as all measurements are repeated this should not
be a problem.

Base-line shifts is a problem (if they exist). It is very important to have a
good base-line before the measurement starts. The 1 µW base-line shift
used in the calculations is a quite high base-line shift if compared with
the noise and slope of the best base-lines seen during our measurements.

Base-line slope is probably not a problem in the way calculated, as it is
difficult to see why one should have a constant slope during 48 h. The
errors are quite small, except for the sorption enthalpy at the end of
the measurement.

Calibration coefficients must of course be well-known. The 1%-case is
probably quite realistic for the SORP4 today, as we have difficulties
in assessing the influences from the calibration copper wires. For this
case we get a higher α-error than the above limit during the first part
of the measurement.

Error in $P_{\text{max}}$ will only affect the calculation of the activity. The 1%-case
is probably realistic and will give higher errors than the limit. Better
measurements of $P_{\text{max}}$ are neccessary.

Cross-talk is not a problem in the present instrument (the cross-talks are
less than 1%).

7  Acknowledgements

I thank Nils and Dorthi Troëdsson Research Fundation for supporting this
study.

8  References

Christensen, G.N. and Kelsey, K. (1959), Holz Roh- Werkstoff 17(5) 189-203

Appendix A: the result
The diagram shows the vapor activity error over a range of vapor activity from 0 to 1. The error is expressed in different units: vapor act. error (top), vapor cont. error (middle), and diff. heat error (bottom). The y-axis on the left represents different magnitudes of error, ranging from $10^{-4}$ to 50. The x-axis represents vapor activity (no error added).
0.3 0.4 0.5 0.6 0.7 vapor activity (no error added)

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

x 10^{-3}

x 10^{-6}

vapor activity (no error added)
vap. cont. error, g/g

vapor activity (no error added)

vap. act. error

diff. heat error, J/g
err2b linear

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
err2b hydrate

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
err3a sigmoid

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
Graphs showing vapor activity, vapor cont. error, and diff. heat error for err3b hydrate, with vapor activity (no error added) on the x-axis and various error metrics on the y-axis.
err5a linear

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
errs sigmoid

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
err5α hydrate

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
err6a sigmoid

vap. act. error

$10^{-4}$

vap. cont. error, g/g

$10^{-4}$

diff. heat error, J/g

vapor activity (no error added)
err6a hydrate

vap. act. err.

vap. cont. err., g/g

diff. heat err., J/g

vapor activity (no error added)
err6b sigmoid

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
err7b linear

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
err7b hydrate

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
err8b sigmoid

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
err8c sigmoid

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
err8c hydrate

vap. act. error

vap. cont. err. g/g

diff. heat error, J/g

vapor activity (no error added)
err9b linear

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
The image contains a graph with the title "err9b sigmoid". The graph is divided into three sub-plots. The top sub-plot represents the vapor activity error, the middle sub-plot represents the vapor content error, both on a logarithmic scale ranging from $10^{-4}$ to 1, and the bottom sub-plot represents the differential heat error, ranging from 35 to 25, on a linear scale. The x-axis of all sub-plots represents the vapor activity (no error added), ranging from 0 to 1. The y-axis of the top and middle sub-plots is labeled as 'vap. act. error' and 'vap. cont. error, g/g' respectively, while the y-axis of the bottom sub-plot is labeled as 'diff. heat error, J/g'.
err9b hydrate

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
err10b sigmoid

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
err10c sigmoid

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
err11a linear

vap. act. error

$10^{-3}$

vap. cont. error, g/g

$10^{-4}$

diff. heat error, J/g

vapor activity (no error added)
err11a sigmoid

vap. act. error

$v \times 10^{-3}$

vap. cont. error, g/g

$4 \times 10^{-4}$

diff. heat error, J/g

vapor activity (no error added)
err11a hydrate

vap. act. error

vap. cont. error, g/g

diff. heat error, J/g

vapor activity (no error added)
err11b linear

vap. act. error

$-0.015 \times 10^{-3} \to 0$

vap. cont. error, g/g

$0 \to 4$

diff. heat error, J/g

$30 \to 0$

vapor activity (no error added)
Appendix B: the computer programs used

Program err1a.m

% err1a short term noise as measured

inps4s
errcase='short term noise'
Pv=Pv+0.1e-6*randn(size(Pv));
Ps=Ps+0.1e-6*randn(size(Ps));

[t,Pv,Ps,as,cs,Dsh]=evalscf('master4e',t,Pv,Ps);

figure(1)
cf
plot(anoe,cnoe,'-r')
hold on
plot(as,cs,'--')
hold off
xlabel('vapor activity')
ylabel('vapor content , g/g')
title(['SORP4 error analysis: ',iso,' tested with ',errcase])

figure(2)
cf
plot(cnoe,Dshnoe,'-g')
hold on
plot(cs,Dsh,'-J')
hold off
xlabel('vapor content , g/g')
ylabel('differential heat of sorption , J/g')
title(['SORP4 error analysis: ',iso,' tested with ',errcase])

Program: inps4s.m

% inps4s
% linres, sigres, hydres are results from simulations
% linene, sigene, hydene are the above files evaluated
% with no errors added

clear
type=input('Which 4s simulation? (lin=1, sig=2, hyd=3)');
addpl=input('Add plot? (yes=1)');
if type==1
load linene
tnoe=t; cnoe=cs; a noe=as; Dshnoe=Dsh; %Pvnoe=Pv; Psnoe=Ps;
load linres
iso='linear isotherm';
elseif type==2
load sigene
tnoe=t; cnoe=cs; a noe=as; Dshnoe=Dsh; %Pvnoe=Pv; Psnoe=Ps;
load sigres
iso='sigmoid isotherm';
elseif type==3
load hydenc
tnoe=cnoe=cs;anoe=as;Dshnoe=Dsh; %Pvnoe=Pv;Psnoe=Ps;
load hydres
iso='hydrate isotherm';
end
disp(iso)
disp('Evaluated case with no error: tnoe, cnoe, anoe, Dshnoe, Pvnoe, Psnoe')

disp('')
disp('AFTER RUN:')
disp('In memory: anoe, cnoe, Dshnoe (noe=no error)')
disp(' as, cs, Dsh (evaluated with error)')
disp(' also, ciso, hhhh (start (true) data)')

---

Program: err.m

% err
% a label for the plots should be in 'namn'

subplot(311)
plot(anoe,anoe-as);
%xlabel('vapor activity (noe)')
ylabel('vap. act. error')
title(namn)

subplot(312)
plot(anoe,cnoe-cs);
%xlabel('vapor activity (noe)')
ylabel('vap. cont. error, g/g')

subplot(313)
plot(anoe,Dshnoe-Dsh);
xlabel('vapor activity (no error added)')
ylabel('diff. heat error, J/g')

---

Program: s4s.m

% sorp4si - a one-dimensional simulation of
% the vapor transport and sorption in SORP4
% for the testing of the influence of errors
% This MATLAB 4 program simulates a measurement with the sorption microcalorimeter
% SORP4 (not the sorption enthalpies...). The following input is asked for by the program:
% h
% rho
% delta
% n
% height of the sample (mm)
density of the sample (mg)
ratio of the diff. coeffs in sample and in air
number of calculation layers in sample
% tend end of simulation (s)
% tout time interval between outputs (s)
% If you give no input the following standard input will be used:
% h=2 mm, rho=0.15 g/cm³, delta=0.5 (M=37 mg), n=5, tend=20000, tout=200, linear isotherm.
% It is also possible for the user to make other changes in the program:
% vsat, psat, Dpair properties of vapor in air
% As surface area of sample (m²)
% Dvh vaporization enthalpy (J/g)
% aiso, ciso, hhhh sorption isotherm & enthalpy
% C, k capacities & conductancies of model
% a(1) activity at vaporization surface
% A simulation gives the following numerical output (+a number of plots):
% t, a, Da activity in each computational cell (1) [a matrix]
% cv apparent concentration in sample (g/g) [a vector]
% Pv, Ps thermal power of vaporization and sorption (W) [vectors]
% The following points should be noted:
% The simulation is by simple forward differences (Fick's law and mass
% balances are calculated in small time increments). The time step dt is
% automatically calculated as the maximum time step found in any part of the
% model at each time
% During the simulation t, a and c are used and the output is stored in
% t, aa and cc. After the simulation the result is transferred to
% in Pv and Ps.
% Calculations are made with SI-units: g, m, s, Pa
% Standard temperature is 25°C and the vapor forming liquid is water
% For each cell only the activity (a) is saved, but as equilibrium is
% assumed the vapor concentration can be found with the sorption isotherm

%-----------------------physical data-----------------------
vsat=23; %vapor content (g/m³)
psat=3160; %vapor pressure (Pa)
Dpair=182e-9; %diffusion coefficient of water vapor in air (g/Pa/m/s)
As=130e-6; %cross sectional area of sample (m²)
Dvh=2440; %heat of vaporization (J/g)
Fmax=400e-9; %maximal vapor flow (g/s)
%fdr=0.9; %time step factor
h=input('height of sample (mm) ':);if (h==0||(h==[]));h=2;end;h=h/1000; %m
rho=input('density of sample (g/cm3) ':);if (rho==[])||(rho==0);rho=0.2;end;rho=rho*1e6; %g/m³
delta=input('Dp(sample)/Dp(air) ':);if (delta==0)|(delta==[]);delta=0.5;end;M=heho;rho;
disp(' ');disp(['Sample mass = ',num2str(M*1e3),' mg']);
n=input('number of calculation layers in sample ':);if (n==0)|(n==[]);n=5;end;
tend=input('end of simulation (s) ':);if (tend==0)|(tend==[]);tend=24*3600;end
tout=input('time interval between outputs (s) ':);if (tout==0)|(tout==[]);tout=5;end
%------------------------sample data------------------------
isoymeal=type of isotherm ? (1=linear, 2=sigmoid, 3=hydrate) :
%also are the activity knickpoints on isotherm
%ciso are the concentration knickpoints on isotherm (g/g)
%hhhh are the differential heats of sorption (J/g(water))
if (type==0)|(type==[]);type=1;end
%standard case
if type==0 %linear
 tiso=[0 1];ciso=[0 0.3];hhh=[-1000 0];
elseif isotype==2 %sigmoid (wood Eucalyptus regnans, Christensen & Kelsey 1959)
    aiso=[0.05 0.10 0.40 0.70 0.80 0.90 0.95 1.00];
    ciso=[0.02 0.035 0.085 0.15 0.18 0.23 0.27 0.37];
    hhhh=[265 200 160 90 45 28 13 5]*(-4.18);
elseif isotype==3 %ohydrate (Morphine sulphate)
    aiso=[0 0.02 0.03 0.085 0.15 0.18 0.23 0.27 0.37];
    ciso=[0 0.0001 0.0538 0.0539 0.135 0.136 0.2];
    hhhh=[0 -22 -22 -8 -8 7 8]*1e3/18;
end
xi=diff(ciso)./diff(aiso); %slope of isotherm
ix=diff(aiso)./diff(ciso): %inverse xi

figure(1);clf
subplot(221)
plot(aiso,ciso,'*');hold on;plot(aiso,cise,'J'),hold off
xlabel('relative activity');ylabel('vapor content (g/g)')
subplot(223)
plot(aiso,hhhh,'*');hold on;plot(aiso,hlhh,'-');hold off
xlabel('relative activity');ylabel('enthalpy (J/gw)')
subplot(122)
text(0,5,\['sample density:',num2str(rho), 'kg/m3'] );
text(0,4,\['sample height=',num2str(h*1000), 'mm'] );
text(0,3,fsample mass='.num2str(M*1e6), 'mg');
text(0,2,l'diff. ratio=',num2str(delta)l)
text(0,1,\[int2str(n), 'simulation cells']);
text(0.0,\['simulation ends at',num2str(tend), 's']);
text(O,-1,\['output interval:',num2str(tout), 's']);
axis([-1 10 -2 5]);set(gca,'Visible','Off')
disp('Press any key to continue (Ctrl-c to abort)');pause

nn=l+n+n; %number of last active conductance in sample
Va=0.72e-6;Vb=1.43e-6;
asim=0.105;
Ra=(1-asim)/8/Fmax;Rb=asim/2/Fmax;Rc=h/2/n/delta/Dpair/psat/As;
k=zeros([1 nn+1]);
C=zeros([1 nn+1]);
a(1)=1; %activity of water
a(1)=1; %activity of water
c=zeros([1 nn+1]); %concentrations
q=zeros([1 nn+1]); %flows (kg/s)
Qv=0; %Q keeps track of the apparent flow since last output (g/s)
dt=fdt/min(C(2:nn)./(k(1:nn-1)+k(2:nn))); %max time step
tdisp=min([tend/20 3600]);
plustdisp=tdisp;
t=0; %time in simulation (s)
amaxend=0; %maximal possible activity
amaxend=0; %when amaxend=1 the simulation has to be stopped
touttext=tout; %second output time (first is at t=0)
leg=ones([1 nn]); %part on isotherm in which each sample part is at each time
out=1; %counter for outputs
nout=ceil(tend/tout)+1; %approx. no of outputs
tt=zeros([nout 1]); % in tt the sim. time is saved
aa=zeros([nout nn]); % in aa the activities are saved
aa(1,1)=1; % activity of source=1 from t=0
cc=zeros([nout nn]); % in cc the activities are saved
da=zeros([1 nn]);dc=da;
cv=zeros([1 1]); % in cv the apparent concentrations are saved
Da=zeros([nout 1]); % in Da the activity difference over the sample is saved
Pv=zeros([nout 1]); % in Pv the thermal power of vap. are saved
Ps=zeros([nout 1]);
konst=1.05*dt/C(7); % to make the simulation run faster
%---------------------- simulation -------------------
tic
disp(['simulation started with dt=',num2str(dt),', s']);
while (t<end)&(amaxend==0)
    t=t+dt; % increment time
    q(1:nn)=(a(1:nn)-a(2:nn+1)).*k(1:nn); % calculate flows
    if (a(7)+konst*q(6)-q(7))>amax;amaxend=1;disp('end of isol. reached');end % stop before going outside isotherm
    da(2:nn)=dt.*(q(1:nn)-q(2:nn))./C(2:nn); % calculate differences in activities
    ind=findstr(int2str((a(7:nn)+da(7:nn))>aiso(leg+1)),','); % find index of sample cells that has changed leg on isotherm
    if ind=[]; t=t-dt;
        dt1=(aiso(leg(ind+1))-a(ind+6))./(q(ind+5)-q(ind+6)).*C(ind+6);
        indx=min(findones(size(dt1))*min(dt1)==dt1);
        dt=dt1(indx);
        t=t+dt;
        da(2:nn)=dt.*(q(1:nn)-q(2:nn))./C(2:nn); % calculate new differences in activities
    end
    Qv=Qv+q(1)*dt; % add flow rate from liquid
    dc(2:nn)=dt.*(q(1:nn)-q(2:nn));
    c(2:6)=c(2:6)./C(2:6);
    a(7:nn)=aiso(leg)+ix(leg).*c(7:nn)/(M/n)-ciso(leg);
    if toutnext<t % time for output?
        if tdisp<
            tdisp=tdisp+plustdisp;
            disp(['t=',num2str(t/3600),', h with dt=',num2str(dt),', s ('num2str(t/tend*100),',%)']);
        end
        out=out+1; % index in output vectors
        t(out)=t; % output time
        aa(out,1:nn+1)=a(1:nn+1);Da(out)=(a(7)-a(nn))*n(n-1);
        cc(out,1:nn+1)=c(1:nn+1)/(M/n);
        cv(out)=cv(out)+1+Qv/M;Qv=0;
        Pv(out)=q(1)*Dvh;
        Ps(out)=1-sum((q(6:nn)-q(7:nn)).*(interpl(aiso,hhhh,a(7:nn))-Dvh))';
        toutnext=toutnext+tout; % time for next output
    end
    if ind=[] % one part entering new leg
        leg(ind(indx))=leg(ind(indx))+1;C(ind(indx))=M/n*xi(leg(ind(indx)));
        disp(['C(',int2str(ind(indx)*6),')=',num2str(C(ind(indx)))]);
        %disp(['C(',int2str(ind(indx)*6),')=',num2str(C(ind(indx)))+6]);
        dt=dt*min(C(2:nn)./(k(1:nn-1)+k(2:nn)));
    end
end
toc
%---------------------- clean up -------------------
tic
L=length(tt); % L=length of vectors
if out<L %clear the unused parts of aa, cc, Pv, tt
    aa(:,out+1:L)=[ ]; cc(out+1:L)=[ ]; tt(out+1:L)=[ ]; Pv(out+1:L)=[ ]; Ps(out+1:L)=[ ];
end

a=aa(:,out+1:L); cc=cc(out+1:L); Pv=Pv(out+1:L); Ps=Ps(out+1:L); tt=tt;
%output is in t, a, cv, Pv and Ps

tt=linspace(0,tout* length(t)-1),length(t))';

for k=1:nn; disp(['Interpolating in a(:,',int2str(k),')']); a(:,k)=interpx(t,a(:,k),tt); end;
for k=1:nn; disp(['Interpolating in c(:,',int2str(k),')']); c(:,k)=interpx(t,c(:,k),tt); end;
disp('Interpolating cv, Pv, Ps, Da');

cv=interpx(t,cv,tt);
Pv=interpx(t,Pv,tt);
Ps=interpx(t,Ps,tt);
Da=interpx(t, Da,tt);

t=tt;
%clear aa cc tt %clear the simulation var. to save space

toc

Function [t,Pv,Ps,as,cs,Dsh]=evalscf(masterfilename,t,Pv,Ps,Pmaxfact)

Program evalscf.m

function [t,Pv,Ps,as,cs,Dsh]=evalscf(masterfilename,t,Pv,Ps,Pmaxfact)
% EVALSCF  An function that evaluates measurements with the Lund
Sorption Calorimeter.

function [t,Pv,Ps,as,cs,Dsh]=evalscf(masterfilename,t,Pv,Ps,Pmaxfact)

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filem=masterfilename; %input('Enter name of m-file with input data (e.g. "indata") : ');
eval(filen); %inputs neccessary data for the evaluation

%-------------------------------------Pv-evaluation--------------------------
if Pv_source==2
    [t dt U t]=filinaf(filev);
    U=subbl(U,1);
    if (te<0)(te==[]) te=findte(t,U,1,'injection');
    end
    ind=round(te/dt);
    t=t(ind:length(t))-te;
    U=U(ind:length(U));
    Pv=tian(t,U,epv,tav,TUv,TdUv); %Pv is the thermal power of vaporization
else
    if Pv_source==1 %Pv already in memory
        dt=(t(2)-t(1));
    end
    if mean(Pv)>0 %it is assumed that endo. Pv is less than zero
        Pv=-Pv;
    end
    if corr1==1
        eval(incofile) %initial correction (tc, Pciv, tendic)
        tt=dt:dt:tendic;
        L=length(tt);
        P_init_saved=Pv(1:L);
        f=Pv(L)/Pciv(length(Pciv));
        Pv(1:L)=interp1(tci,Pciv,tt,'spline')*f;
    end
    if glycerol==0
        qv=-Pv/Dvh;
    else
        [qv,av,Dvh]=corrglyc(Pv,Vgw,cgw); %correction for g-w mix
    end
    if corr2==0
        as=av-qv/Pmax.*Dvh; %as is the vapor pressure of the sorbing sample
        qs=qv;
    else
        %correction for sorption time lag
        [as,qs]=corrstl(k1,k2,k3,c12,C23,t,qv,av);
    end
    if corr1==1 %If a initial correction has been made...
        as(1:L)=as(L+1)*ones([1 L]);
    end
    cs=(m0-mdry)/mdry+cumsum(qs)*dt/mdry;
    subplot(121)
    %plot(as,cs,')
    %axis([0 1 0 1.05*max(cs)]);
    %xlabel('relative vapor activity')
    %ylabel('vapor concentration (g_vapor/g_dry_sample)')
    %title(filev)
    var_str1='t dt U Pv F as cs';
    %-------------------------------------Ps-evaluation--------------------------
    if Ps_source==0
    if Ps_source==2


[t dt U tx]=filinaf(files);
U=subbl(U,1);
t=t(ind:length(t))-te;
U=U(ind:length(U));
Ps=tian(t,U,eps,ta,TUs,TdUs);

elseif Ps_source==1

Ps is the thermal power of sorption

elseif Ps already in memory
end

if length(Ps)>length(Pv)
Ps=Ps(1:length(Pv));
elseif length(Ps)<length(Pv)
Pv=Ps(1:length(Ps));
end

t=t(1:length(Ps));
if mean(Ps)<0 %In the equations it is assumed that

%the exothermic Ps is greater than zero

Ps=-Ps;
end

Dsh=(Ps./Pv+1)*Dvh; %dsh is the sorption enthalpy liquid-->sorbed phase (<0)

% subplot(122)
% plot(as,Dsh,')
% %axis((0 1 0 1.05*max(cs))):
% xlabel('relative vapor activity')
% ylabel('sorption enthalpy liquid-->sorbed phase (J/g_vapor)')
% title(files)
% var_str2='Ps, Dsh';
else

var_str2=""
end

disp('-----------------------------------------------')
disp(['Variables ','var_str1.var_str2,' are left in memory'])
disp('-----------------------------------------------')

Program file: master4e.m

%MASTER4E
%Master file for indata to EVALSC for ERROR ANALYSIS
%
%Lars Wadsø January 8, 1997, 970918, 971010
%
% v vaporization
% s sorption

%----FILES vaporization-----------------------------
Pv_source=1; %if Pv_source==1 : t, Pv are in memory
%if Pv_source==2 : input from file ("filev")
%file='c:\measurem\cmc\ntestb.061';
%if file='error anal.1';
%if Pv_source==1 "filev" will be used as title in plot
%----FILES sorption-----------------------------
Ps_source=1; %if Ps_source==0 : no evaluation of sorption mea.
%if Ps_source==1 : t, Ps are in memory
%if Ps_source==2 : input from file ("files")
files='c:\measurem\cmc\ntestt.061';
files='error anal.';
if Ps_source==1 "files" will be used as title in plot
CORRECTIONS--(if corr1==1 correction x will be made)--
corr1=1; %initial
corr2=0; %sorption time lag
glycerol=0; %glycerol-water mixture
PARAMETERS----------------------------------
m0=52e-3; % initial and dry weight of sample (g)
mdry=m0;
TEXT_date='8 jan 1997';
TEXT_temp='25oC';
TEXT_calorim='SORP4';
TEXT_sample='Fiber board (Burch) dried over CaCl2';
TEXT_vapor='Water (millipore)';
epv=0.096529e-6;
tav=144;
epss=0.124069e-6;
tas=131;
TUV=20;TdUv=20;TDUs=20;TdUg=20;
Dvh=2440; %dvh is the enthalpy of vaporisation (J/g)
Pmax=975e-6; % Pmax is the maximal thermal power (W)
if exist('Pmaxfact')
    Pmax=Pmax*Pmaxfact
    Pmaxfact=[];
end
activity of vapor
tc=0; %time of injection (give tc<0 if not known)
CORRECTION: build-up of initial gradient---
if corr1==1
    incofile='incos4';
end
CORRECTION: correction for time-lag of sorption---
if corr2==1
    vSAT=23;
    qmax=Pmax/Dvh;
    A=4.54e-5;
    V=1.43e-6;
    L=64e-3;
    act=0.885;
    k1=qmax/(act/2);
    k2=k1;
    k3=qmax/(1-act);
    C12=vSAT*3/4*A*L;
    C23=vSAT*(V+1/4*A*L);
end
CORRECTION: glycerol-water mixture--------
if glycerol==1
    Vgw=1e-6; %initial volume of glycerol-water mixture (m3)
    cgw=0.5; %initial concentration of glycerol-water mixture (%glyc.)
end

this was used for the error analysis!
not applied for error analysis!
not applied for error analysis!