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Initial correction for the SORP4 sorption microcalorimeter

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1 Nomenclature

The following nomenclature is used:

a	vapor activity ($=p/p_{\mathrm{sat}}$)	Pa/Pa
c	vapor content	g/g
f	factor (Eq. 4)	1
M	dry sample weight	g
P_{s}	measured thermal power of sorption	W
P_{v}	measured thermal power of vaporization	W
$\tilde{P}_{\mathrm{v}}$	simulated effective thermal power of vaporization	W
P_{max}	maximal P_{v}	W
t	time	s
t_{e}	end of measurement	s
t_{c}	end of initial correction	s
$\Delta_{\mathrm{s}}h$	sorption enthalpy	J/g
$\Delta_{\mathrm{v}}h$	vaporization enthalpy	J/g

In the present report the following sign-conventions are used:

$$\begin{aligned} P_{\mathrm{s}} &> 0 \\ P_{\mathrm{v}} &> 0 \\ \Delta_{\mathrm{s}}h &< 0 \text{ (in most cases)} \\ \Delta_{\mathrm{v}}h &> 0 \end{aligned}$$

The enthalpy of sorption, $\Delta_{\mathrm{s}}h$, is usually less than zero, but for some cases with strong entropy effects it may be greater than zero.

2 Introduction

The SORP4 sorption microcalorimeter is an instrument to measure sorption isotherms and sorption enthalpies. A measurement is conducted by placing a dry sample in a sorption chamber and introducing a vaporizing liquid to a vaporization chamber. The two chambers are connected by a tube that governs the rate of diffusion from the liquid to the sample. During a measurement the initially dry sample will sorb vapor and increase its vapor activity and vapor content. The vaporization-sorption vessel is placed in a double twin microcalorimeter so that the thermal powers of the vaporization and sorption processes may be measured independently. From these calorimetric measurements as a function of time the sorption isotherm and the enthalpy of sorption may be evaluated by the following equations (the nomenclature is given above):

$$a = 1 - \frac{P_\mathrm{v}}{P_\mathrm{max}} \tag{1}$$

$$c = \frac{1}{M \cdot \Delta_\mathrm{v} h} \int_0^t P_\mathrm{v}(\tau)\mathrm{d}\tau \tag{2}$$

$$\Delta_\mathrm{s} h = \Delta_\mathrm{v} h \cdot (1 - \frac{P_\mathrm{s}}{P_\mathrm{v}}) \tag{3}$$

Read Wadsö (1996, 1997) for more detailed descriptions of the instrument and the method.

3 The need for an initial correction procedure

The measurement is started by the introduction of a vaporizing liquid into the calorimeter. In SORP4 the introduction is by an injection with a precision syringe pump. In future versions of the SORP-instruments the measurements will probably be started by the opening of a valve to expose the vaporizing liquid. Independent of how the measurement is started we have a problem in evaluating the initial phase of the measurements.

Figures 1 and 2 show the thermal powers of sorption and vaporization from sixteen SORP4 measurements with cellulose derivatives. The following details may be noted:

- The thermal powers of vaporization all show a high initial peak that is caused by the evaporation of the first injected water into the initially dry air in the vessel. After about 300 s, however, the initial phase is clearly finished and a quasi steady-state diffusive flow has been established.

- All samples were dried before the start of the measurements and after the initial peaks all thermal powers of vaporization except one are less than $P_{\text{max}} = 0.975$ mW (cf. Eq. 1). The samples showing the highest thermal powers at this stage, e.g. at 300 s, are the ones that can keep their surroundings (the sorption chamber) at the lowest vapor activity. Samples that were not well dried or samples that are so large that their internal diffusion partly determines their rates of sorption will show the lowest thermal powers. It may also be a problem that if the inside of the vessel is not dried to the same extent as the sample; then adorption effects may influence the baselines.

- The disturbances seen in several of the vaporization curves before 300 s are probably caused by the injection that does not stop until 100 μl has been injected after 240 s. During the injection the steel surface that is wetted by the vapor steadily increases, probably in a somewhat erratic fashion.

- Most of the thermal powers of sorption starts to increase approx. 20 s after the injection. This is the time it takes for the first evaporated water to reach the sample. After this the sorption increases rapidly until it, after approx. 150 s, a quasi steady-state is reached.

- A few of the sorption curves either start at high thermal powers or have initial disturbances. This may be caused by the injection needle being wet when it is introduced or that some water escapes from the needle while it passes the sample when it is on its way down to the vaporization chamber. Some types of sample particles may sometimes stick to the upper edge of the tube, or even to the inside of the tube; this will disturb the measurement.

- The spread in the thermal powers of sorption is caused by the same factors as those that affects the thermal power of vaporization (cf. the second point above), but also by differences in enthalpies of sorption between the samples.

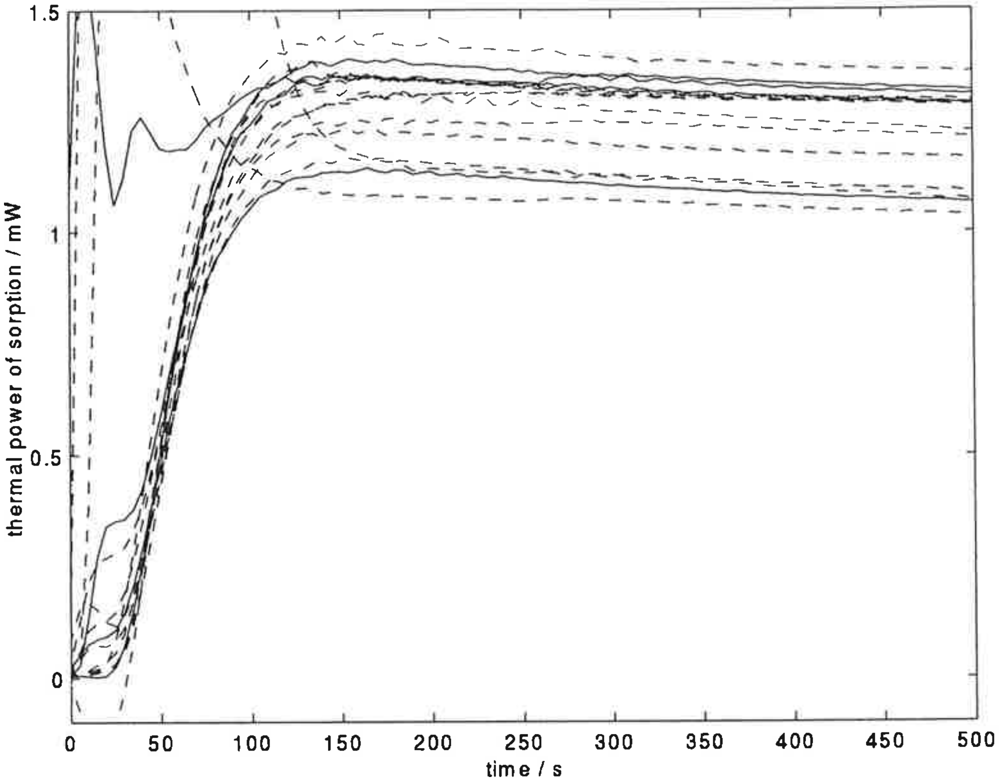

Figure 1: Thermal powers of *sorption* from sixteen measurements. The four solid lines are from measurements on microcrystaline cellulose (MCC), and the twelve dashed lines are from measurements on carboxymethylated cellulose (CMC).

- The thermal powers of vaporization are much more disturbed that the thermal powers of sorption.

We cannot use the initial part of the measured thermal powers of vaporization in Eq. 1 because it includes the effect of the water that evaporates to establish the initial vapor pressure gradient in the vessel, as well as other disturbances from the injection procedure such as wetting of the steel. The main idea of this report is to find a way of exchanging the first part of the measured vaporization curve for a computer simulated curve that better represents the evaporation of liquid that reaches the sorbing sample.

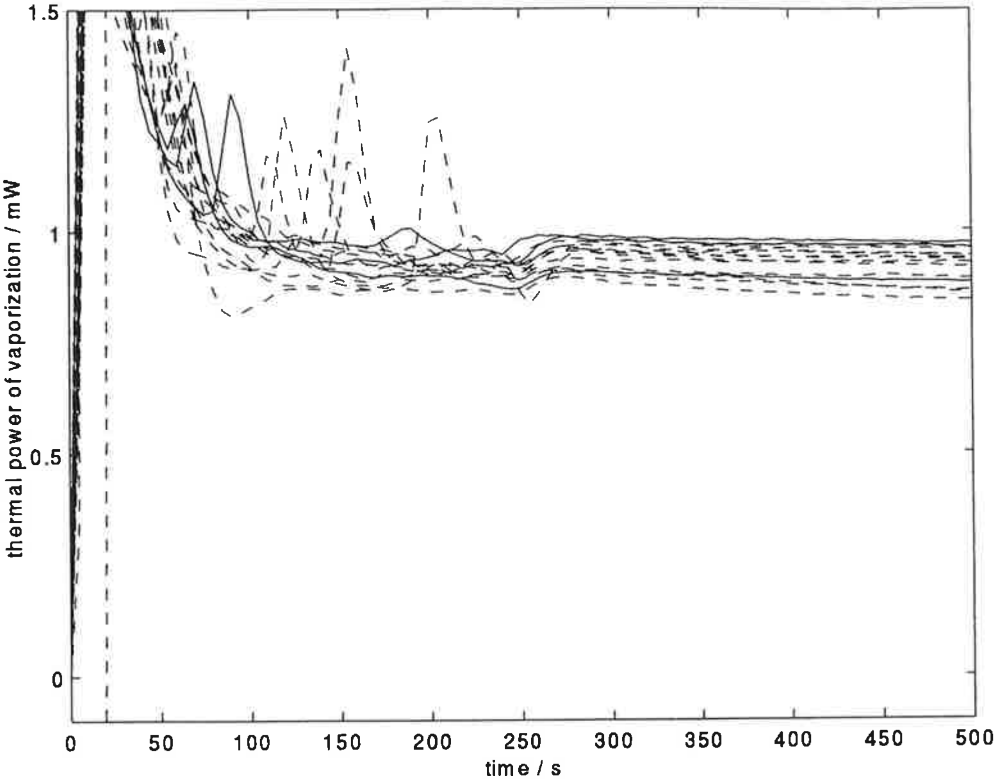

Figure 2: Thermal powers of *vaporization* from sixteen measurements. The four solid lines are from measurements on microcrystaline cellulose (MCC), and the twelve dashed lines are from measurements on carboxymethylated cellulose (CMC).

4 A correction procedure

We call the measured thermal powers P_v and P_s, and the initial simulated curve $\tilde{P}_\mathrm{v}$. The main idea of a correction is that the *initial* thermal power of vaporization (P_v) is not good, and should be replaced by another thermal power of vaporization ($\tilde{P}_\mathrm{v}$) that better represents what happens at the sorbing sample. The following should be noted:

- $\tilde{P}_\mathrm{v}$ is simulated and cannot be better than the simulation model, so one should carefully investigate the properties of the model. The method of initial correction described here does, however, certainly give a much better end-result than if it was not used.

- We refer everything to what is happening on the sorption side, i.e. all corrections are made to make P_v comparable with P_s. Therefore, when we exchange $\tilde{P}_\mathrm{v}$ for P_v for the first part of the measurement there will be no sorption time-lag[1] during this part of the measurement. A time-lag correction should therefore not be applied to the part corrected by the initial correction.

As described above the initial correction is made by exchanging P_v for $\tilde{P}_\mathrm{v}$ for the first part of a measurement. This procedure may be formalized in the following way:

$$P_\mathrm{v}(0...t_\mathrm{e}) \leftarrow f \cdot \tilde{P}_\mathrm{v}(0...t_\mathrm{c}) + P_\mathrm{v}(t_\mathrm{c}...t_\mathrm{e}) \tag{4}$$

Here, three dots (...) indicates time ranges, and the left-arrow (←) symbolizes that what is on right is put into what is on the left (similar to "=" in a computer language). In this way we change the first part of a measured thermal power of vaporization to be more in accordance with the measured thermal power of sorption.

The factor f in Eq. 4 is needed to make the two parts of the new P_v fit together nicely. It is defined by:

$$f = \frac{P_\mathrm{v}(t_\mathrm{c})}{\tilde{P}_\mathrm{v}(t_\mathrm{c})} \tag{5}$$

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[1] The sorption time-lag is caused by the vapor having to diffuse from the vapor source to the sample. As this takes some time an effect in the sample will be seen later and smoothed out in the measurement on the vaporization side. A correction for this is described in a later report in this series.

The end-time of the correction (t_c) should be taken when a quasi steady-state diffusion has been established in the vessel. As seen in Figs 1 and 2 this seems to take 150 s in the sorption chamber and 300 s in the vaporization chamber, and we have no other choice than to wait approx. 300 s until we may use the measured vaporization curve. It is, however, certainly possible to improve the start of the measurement to take away some of the initial disturbances in the vaporization chamber and bring the time of the initial correction down to half of the present value.

According to computer simulations the *shape* of the initial part of P_v is not dependent on the sample at all. It is only the initial vapor activity of the sample that determines the absolute *level* of the thermal powers. Real measurements give another picture; the initial part of P_v is disturbed and it is not possible to use computer simulations to determine when to end the correction (t_c). Below I present three methods to find t_c and their respective merits.

4.1 low slope

One type of rule to find t_c could be to start at t=150 and going forwards in time until

$$|\mathrm{d}P_v/\mathrm{d}t| < \psi \tag{6}$$

where ψ could, based on simulations, be $30 \cdot 10^{-9}$ W/s. However, measured curves are not at all as nice as the simulated ones, and this method is not easy to implement as the time derivatives of measured thermal powers of vaporization are very noisy. As we use the Tian equation to correct for the thermal inertia of the calorimetric vessel the time derivative may be written:

$$\frac{\mathrm{d}P_v}{\mathrm{d}t} = \varepsilon \frac{\mathrm{d}}{\mathrm{d}t}(U_v + \tau \frac{\mathrm{d}U_v}{\mathrm{d}t}) \tag{7}$$

The second order derivatives in this equation cause a lot of noise and make this method impractical.

4.2 fixed time

It is also possible to always use the same t_c. Based on Figs. 1 and 2 t_c=300 s seems to be a reasonable choice. Table 1 gives some evaluated values for four simulated curves. It is of special interest to compare the two last columns for

Table 1: Some evaluated values for four simulated isotherms. The thermal powers P_v have units of μW, and 1-a in the last colum is one minus the activity at which a sample first starts to sorb vapor. The 'linear', 'sigmoid'and 'hydrate' isotherms are described in Wadsö (1997). The 'hydrate 2' is an isotherm that has a low sorption until $a = 0.50$.

curve	P_v	$P_\mathrm{v}/P_\mathrm{max}$	1-a	P_v	$P_\mathrm{v}/P_\mathrm{max}$	1-a
	for $t_\mathrm{c} = 200$s			for $t_\mathrm{c} = 300$s		
linear	974.2	0.999	1.000	969.9	0.995	1.000
sigmoid	974.9	1.000	1.000	971.2	0.996	1.000
hydrate	948.9	0.973	0.973	946.8	0.971	0.971
hydrate 2	517.0	0.530	0.500	488.1	0.501	0.500

each time, because, according to Eq. 1 $P_\mathrm{v}(t)/P_\mathrm{max} = 1 - a(t)$. It is seen that the values compare very well. Both 200 and 300 s seems to be good values of t_c. In practice, however, 300 s is the best.

4.3 user decides

A third method is of course to let the user choose a good t_c based on P_v and P_s. It is then possible for the user to extend the time for the correction if a very noisy and disturbed curve is to be analyzed. It will, however, be difficult to implement such a method for normal users, e.g. in an industrial laboratory.

5 Correction files

A correction file should give the thermal power of vaporization corresponding to the vapor being sorbed in the sample. I have made and tested a number of different correction files.

5.1 3-dimensional simulation

Figure 3 shows the result of a simulation of the initial vapor flow in a SORP4 microcalorimeter. The simulation was made with HEAT2R (Blomberg) by rewriting the problem in dimensionless temperatures (T). At time zero $T = 0$ everywhere in the vessel except at the bottom vaporization surface, where

$T = 1$. The correction file was calculated as the enthalpy of vaporization multiplied by the vapor content increase rate of the sample corresponding to the temperature increase in the simulation. The resulting correction file is called 'incos4.m'.

5.2 1-dimensional simulation with instantaneous vapor source activity

A simple 1-dimensional diffusion simulation with two vapor capacities in the gas phase and one sample vapor capacity (MATLAB program tltest.m in Appendix A) was also tested. The activity of the vapor source was one from the start of the simulation. This was the same boundary conditions as in the 3-dimensional simulation and the result (shown in Fig. 3) is also very similar. Part of the difference seen may be caused by that the 3-dimensional simulation probably was done with slightly different geometrical data. The resulting correction file for this 1-dimensional simulation is called 'incos4b.m'.

5.3 1-dimensional simulation with gradually increasing vapor source activity

As seen in Fig. 3 the measured thermal power of sorption is slightly more delayed then the data in the two correction files that were simulated with an instantaneous liquid surface. A possible cause of this is that the liquid surface in the bottom of the vessel is not immediately formed at time zero because it takes 240 s to titrate the water needed into the bottom vessel (a slow injection is used to not disturb the microcalorimeter). At time zero the first liquid emerges from the tip of the needle. This liquid forms a small drop that after some time contacts the bottom. The stainless steel of the vessel is not very hygrophilic, however, so the bottom is wetted quite slowly. Therefore, I have tried to make a better correction file by changing the boundary condition at the vaporization side.

Figure 4 shows the input and the result of simulations with linearly increasing vapor activity at the vaporization side. The measured curve starts at the 100 s curve and ends at the curve with instantaneous $a_v = 1$, so the fit is not much better than for the previous correction files. The resulting correction files for this 1-dimensional simulation are found in 'incos4c1.mat' to 'incos4c4.mat'.

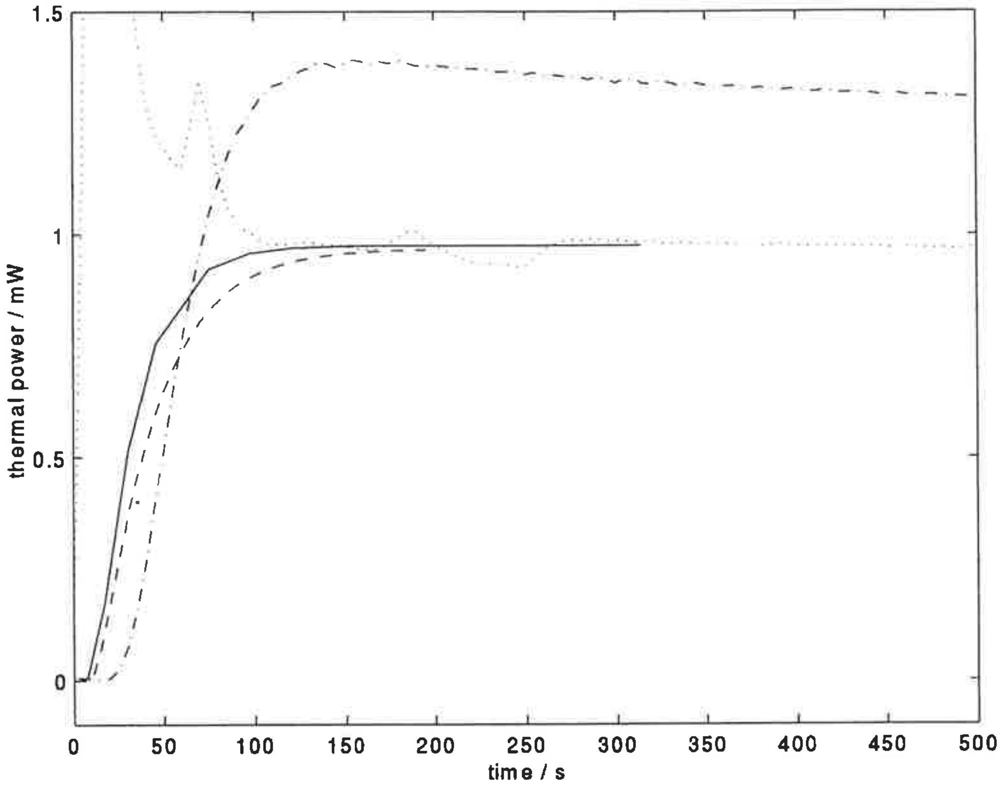

Figure 3: Simulated and measured curves. The solid and dashed lines are the correction files from the 3- and 1-dimensional simulations, respectiviely. The dash-dotted line is a typical measured thermal power of sorption (MCC measurement ntestt.070) and the dotted line is the thermal power of vaporization from the same measurement (ntestb.070).

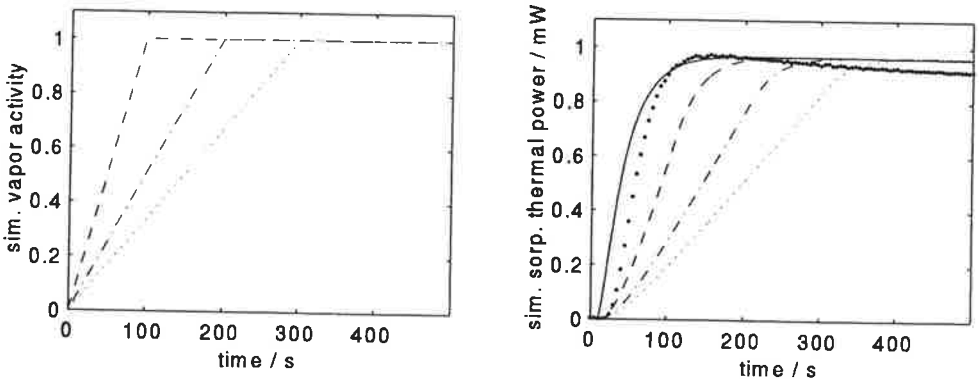

Figure 4: **LEFT:** The three cases of gradually increasing vapor activity on the vaporization side. The time until the vapor activity reached one was 100 s (dashed line), 200 s (dash-dotted line) and 300 s (dotted line). **RIGHT:** The results of the simulations with gradually increasing vapor activity (the lines are the same as in the left side of the figure; the solid line is from a simulation with the activity one from time zero). The curve with large dots is a measured thermal power of sorption (ntestt.070) that has been scaled to have approximately the same maximal thermal power as the simulated curves.

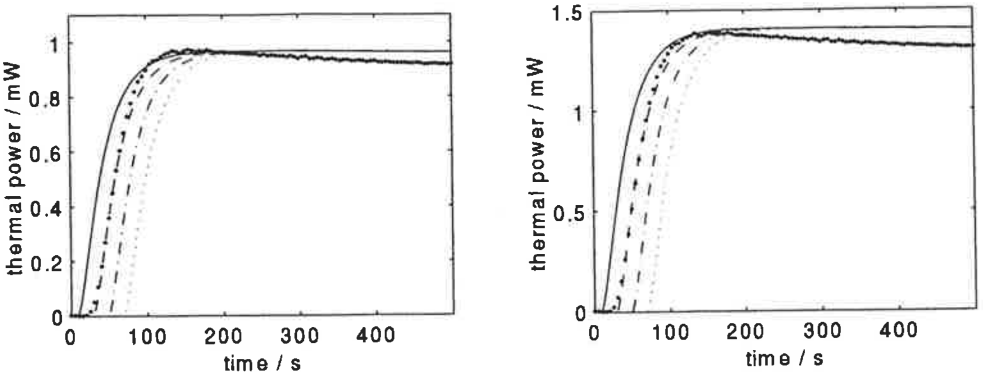

Figure 5: **LEFT:** The results of the simulations with delayed vapor activity increase and a linear isotherm ('linear'). The curves are for delays of 0 s (no delay, solid line), 20 s (dashed line), 40 s (dash-dotted line), and 60 s (dotted line). The curve with large dots is a measured thermal power of sorption (ntestt.070) that has been scaled to have approx. the same maximal thermal power as the simulated curves. **RIGHT:** The same as the left figure, but the simulations were done with a sigmoid (wood) isotherm.

5.4 1-dimensional simulation with delayed vapor source activity

Figure 5 shows the input and the result of simulations with $a_v = 0$ during the first time (after that time $a_v = 1$). This results in a shift of the curves to the right. The simulation with a 20 s delay fits the measured data well and will therefore be used in the following. The resulting correction files for this 1-dimensional simulation are found in 'incos4d1.mat' to 'incos4d4.mat' ('incos4db.mat' is the one that had the best fit; it is also implemented as 'bestinco.m' for use in our evaluation programs).

6 Results and uses of the initial correction

If no initial correction is made the wrong moisture content gain will be found for the whole measurement. To some extent this could have been corrected by the 'sorption time-lag' correction procedure, but there are also other sources of error:

- Wetting of metal surfaces.
- Wrong temperature of injected liquid.
- The liquid surface is not created immediately at t=0.

It is therefore good to have a separate procedure for the initial corrections and only using the 'sorption time-lag' correction for the later part of the measurement when the processes are more well defined and stable.

If an initial correction is applied up to time t_c, at this time we will have calculated values of vapor activity and vapor content (a_c and c_c). Two things should be noted:

- The vapor activity a_c is the activity found at time t_c for the uncorrected P_v-curve[2]. We have not measured the true sample activity at times lower than t_c, and we will therefore have a problem to connect the activity to the origin of the sorption isotherm. Three different solutions to this may be used:
  1. Use a constant vapor activity a_c for all times up to t_c.
  2. Start the sorption isotherm at the point (a_c, c_c).
  3. Draw some kind of straight line from the origin to the point (a_c, c_c).
- The vapor content c_c at time t_c is calculated from the correction file data and is (for one correction file) only a function of t_c and f. Table 2 gives some values of c_c for the three correction files used. In all cases I

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[2] Actually, it is $P_v(t_c)$ that is found, but to simplify the reasoning I here discuss it in terms of a and c.

Table 2: Values of the vapor concentration calculated by Eq. 2 after different times for three correction files and two measured curves (MCC: ntestb.070; CMC: ntestb.059). The calculations were done for $f = 1$ and $M = 52$ mg (also for the measured curves that had weights of 64 mg (MCC) and 14 mg (CMC), respectively).

source of data	calculated vapor contents $c(t)$ / mg/g					
	50 s	100 s	150 s	200 s	250 s	300 s
incos4.m	0.16	0.52	0.90	1.28	1.67	2.05
incos4b.m	0.12	0.45	0.82	1.20	1.58	1.96
incos4d2.m	0.03	0.31	0.67	1.04	1.43	1.81
MCC	0.70	1.15	1.54	1.92	2.29	2.68
CMC	0.85	1.22	1.58	1.92	2.26	2.61

have assumed that $f = 1$ and that the sample mass $M = 52$ mg. Note, however, that ('$\backsim$' is 'proportional to'):

$$c(t) \backsim f$$
$$c(t) \backsim \frac{1}{M}$$

Table 2 give moisture contents in the order of $2{\cdot}10^{-3}$ g/g after 300 s for all the data sources. This is approx. 1% of the moisture content measured for many hygroscopic materials (e.g. wood) at high water activities. The data in Table 2 also show that the difference in vapor content between not using a correction (directly using the measured P_v) and making a correction is approx. $0.8{\cdot}10^{-3}$ g/g. This is not much, but the initial correction not only changes the vapor content, it also gives more realistic vapor activities. An uncorrected P_v will be greater than P_{max} during the initial phase of a measurement and the activities evaluated with Eq. 1 will then take unphysical values less than zero. An applied correction will always be equal to or less than P_{max} and give physically possible vapor activities.

7 Two possibly problematic cases

7.1 Samples with first sorption at $a \ll 1$

If a sample is not dry at the start of the measurement or if it is of a substance that does not absorb anything until a certain vapor activity (a_i), the measured thermal powers will be a factor f lower than had the sample started to sorb at $a_\mathrm{i} = 1$. If it is assumed that the diffusion rate are proportional to the vapor activity difference (Eq. 1), then the following also holds true:

$$f = 1 - a_\mathrm{i} \tag{8}$$

Then the correction procedure may be applied just as for a sample with high a_i and f will be the factor in Eq. 4.

7.2 Samples with only very low sorption

If a sample has a very low vapor capacity there will be no clearly definable a_i and there will never be a horizontal part of P_v where t_c may be taken. Because of this the correction procedure developed here will not work well. This type of situation may be caused by several factors:

Sample size. The samples have to be over a certain size for the measurement technique to work well. As it is the sample itself that determines the sorption rate and a very small sample will not be able to do this; as a result there will be a rapidly decreasing thermal power. For most biomaterials (cellulose derivatives, lipids, cotton, dried apple) the optimal sample size is in the order of 50 mg.

Sample sorption isotherm. If the sorption capacity is extremely low at low vapor activities this will make the measurement much more difficult.

Sample sorption rate. The SORP instruments are not well suited for samples with time dependent sorption (long time scales for internal diffusion or sorption processes) unless one is interested to study the kinetics of the sorption. If it is the internal diffusion that is a problem, try dividing the sample into smaller pieces. The SORP technique works best for fine powders.

- **Vessel adsorption.** The adsorption on the internal stainless steel parts of the vessel may be a problem, but if the above factors are observed the adsorption is probably so low that it will not influence the result.

If a sample shows a continuously decreasing thermal power of vaporization and it is difficult to find a good t_c, then it is probably best to use a low t_c and note that the result may not be as reliable as most measurements are.

8 The error in the vapor gain

At time t_c there will be a certain difference between the vapor contents calculated with a correction and without a correction. From Table 2 we find values of the vapor gain after 300 s. Corrected values for these 52 mg samples are in the order of 2 mg/g and they are about 0.8 mg/g lower than uncorrected values. As I believe that the correction procedure is good, I also believe it is safe to assume that an (undefined) uncertainty in the initial vapor gain for a corrected measurement on a 52 mg sample is within ±0.2 mg/g (but this may have to be further investigated in some way). For a sample with a dry mass of M (g) the corresponding uncertainty in the vapor gain after 300 s is:

$$\pm\frac{0.2\cdot 10^{-3}\cdot 52\cdot 10^{-3}}{M}\approx\frac{\pm 10^{-5}}{M} \tag{9}$$

9 Two examples of the use of the initial correction

Figures 6-11 gives example of uncorrected and corrected data from two measurements. For both cases $t_c = 300$ s and the correction file 'incos4d2' ('bestinco.m')was used. Figures 6-8 are from measurements on a microcrystalline cellulose (MCC) and 9-11 are from measurements on a carboxymethylated cellulose (CMC). The main difference between these measurements is that the CMC sample was much smaller and maybe not dried as well as the MCC sample. Table 3 gives some date showing this. Note that the negative vapor activity ($f > 1$) calculated for the MCC sample was unique in the sixteen measurements tested. For all sixteen measurements the f-values were quite evenly distributed between 0.908 and 1.016. An f-value higher

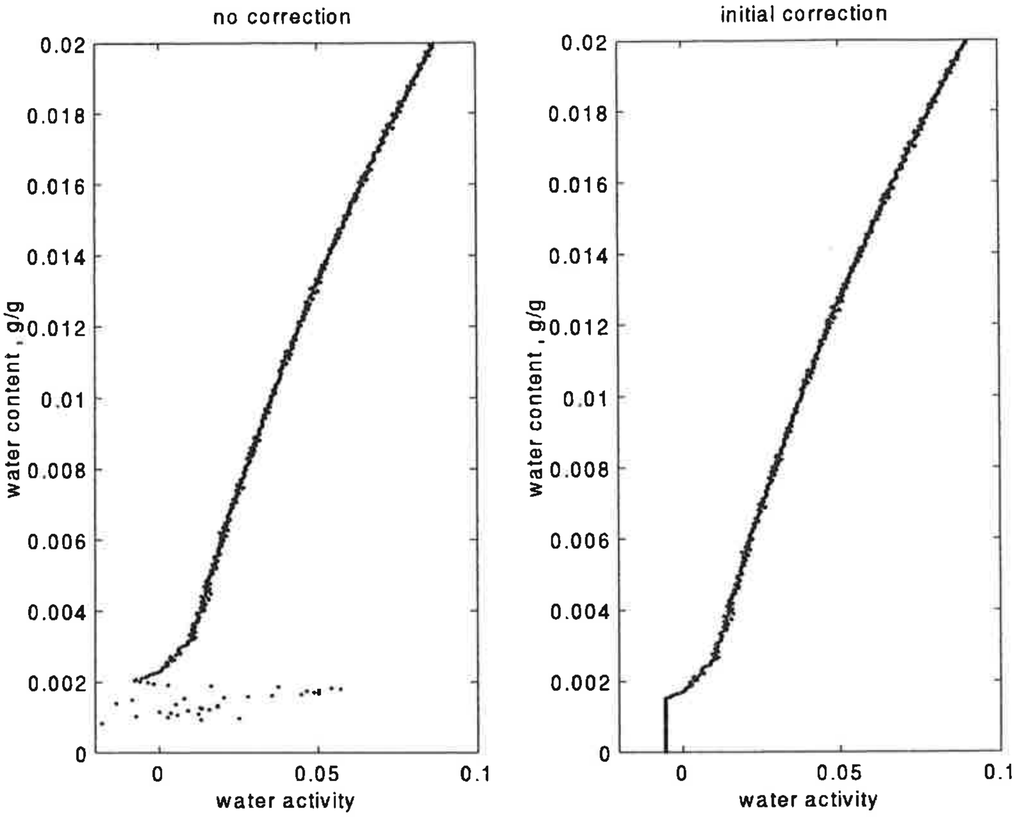

Figure 6: A measurement with a microcaystalline cellulose (MCC, ntest.070). The two solid lines show the measured thermal powers of sorption and vaporization, and the dashed line is the corrected part of the vaporization curve.

than one implies either that P_{max} is too low or that there is an error in the measurement (e.g. an disturbance).

Figures 6 and 9 show that t_c is well chosen as the correction curves removes the disturbed parts of P_v. The other results also show that this results in much better looking sorption isotherms and heats of sorption. However, note the following:

- The initial vertical part on the sorption isotherm is just a way to show that a correction has been made.
- The heats of sorption during the first part of the measurement are probably uncertain as they are calculated by taking the ratio of the thermal power of sorption and the correction curve (cf. Eq. 3).

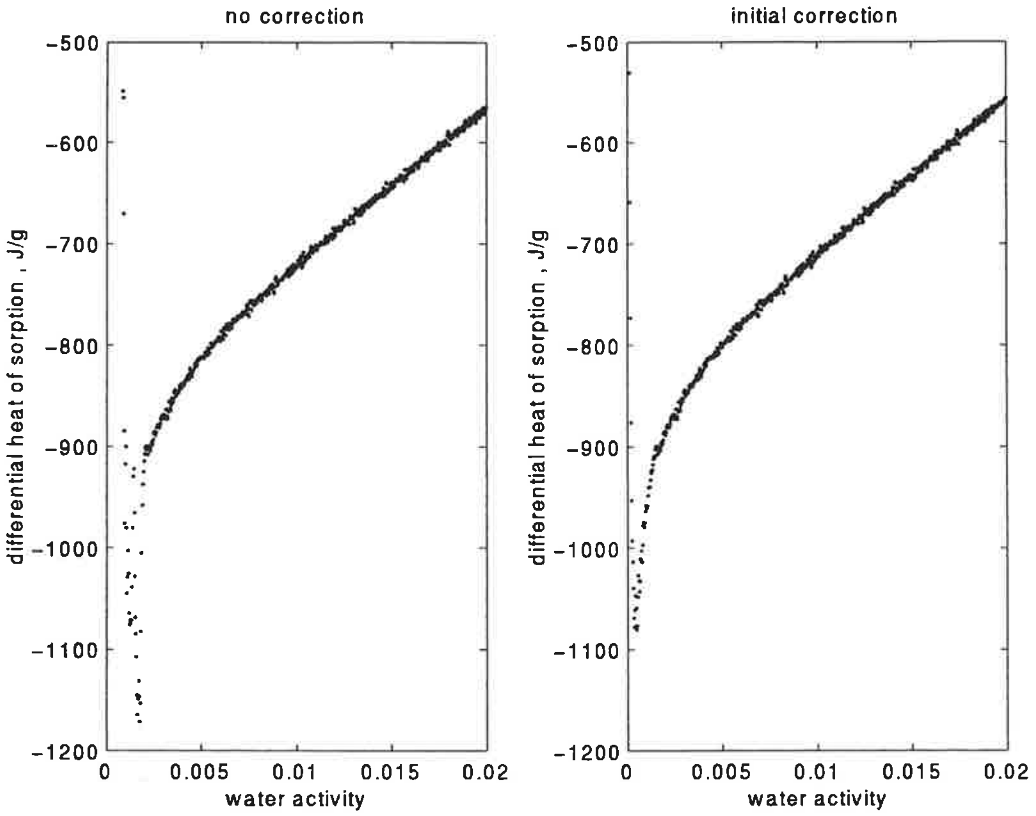

Figure 7: The evaluated sorption isotherms from measurements with a MCC. The left diagram is without correction and the right diagram is with the correction applied.

Table 3: Data from two applications of the initial correction procedure.

sample	file	M / mg	f	$a(t_c)$
MCC	ntest.070	64	1.016	-0.016
CMC	ntest.059	14	0.927	0.073

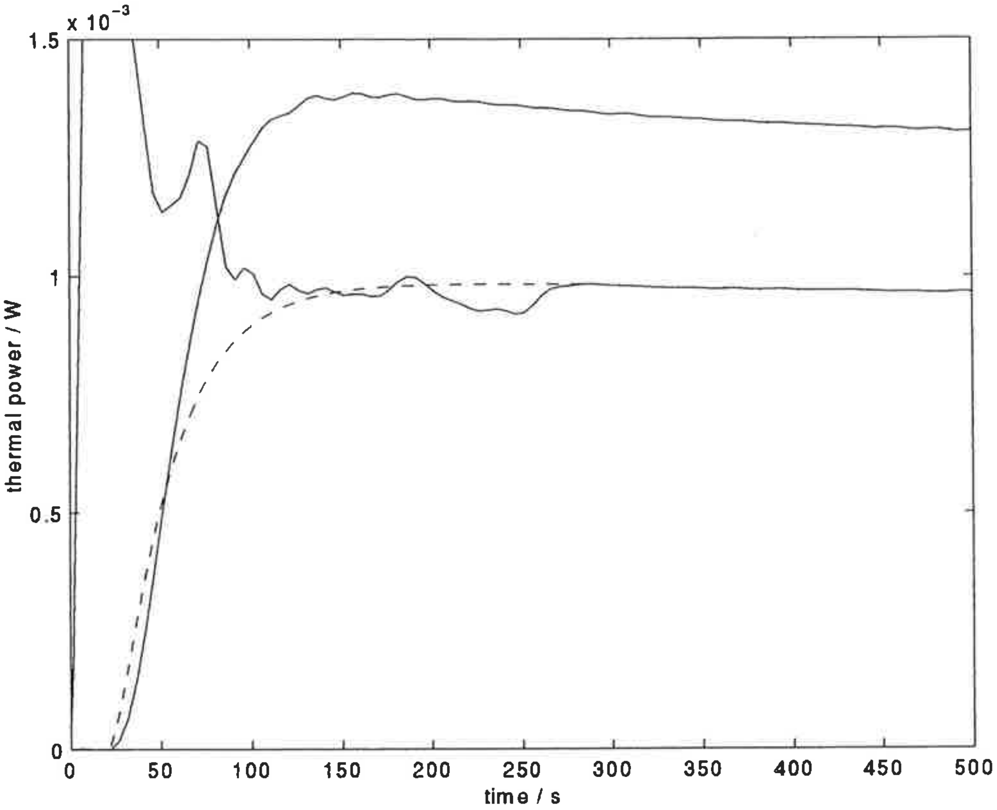

Figure 8: The evaluated heats of sorption from measurements with a MCC. The left diagram is without correction and the right diagram is with the correction applied.

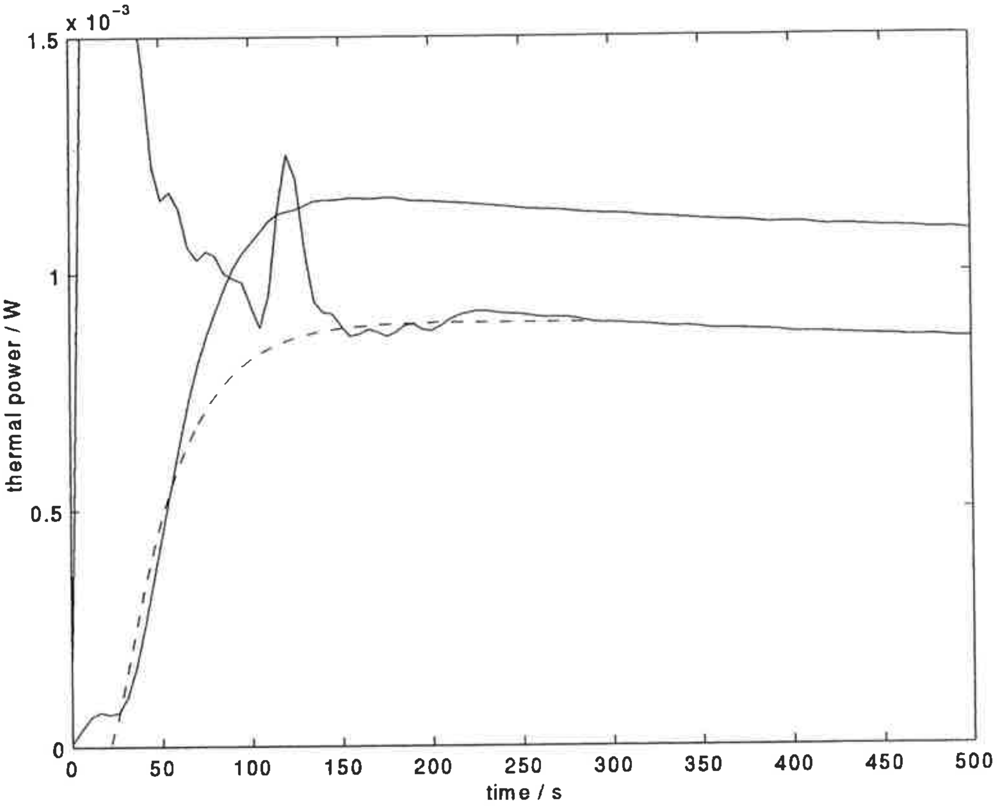

Figure 9: A measurement with a carboxymethylated cellulose (CMC, ntest.059). The two solid lines show the measured thermal powers of sorption and vaporization, and the dashed line is the corrected part of the vaporization curve.

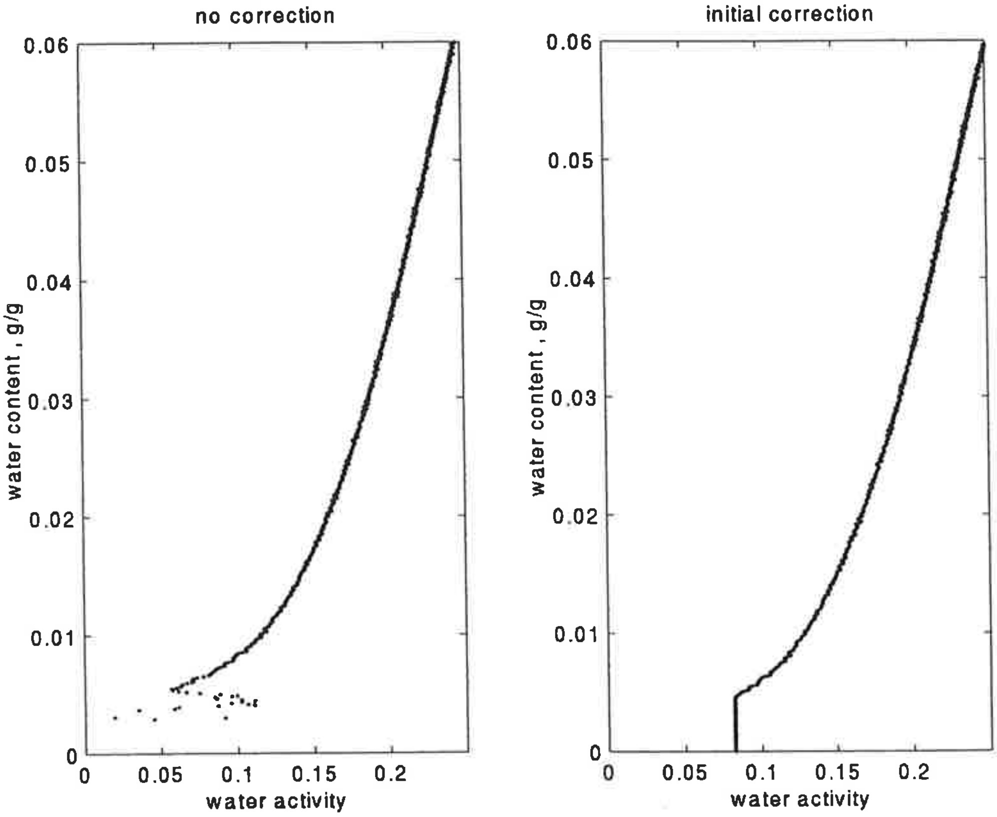

Figure 10: The evaluated sorption isotherms from measurements with a CMC. The left diagram is without correction and the right diagram is with the correction applied.

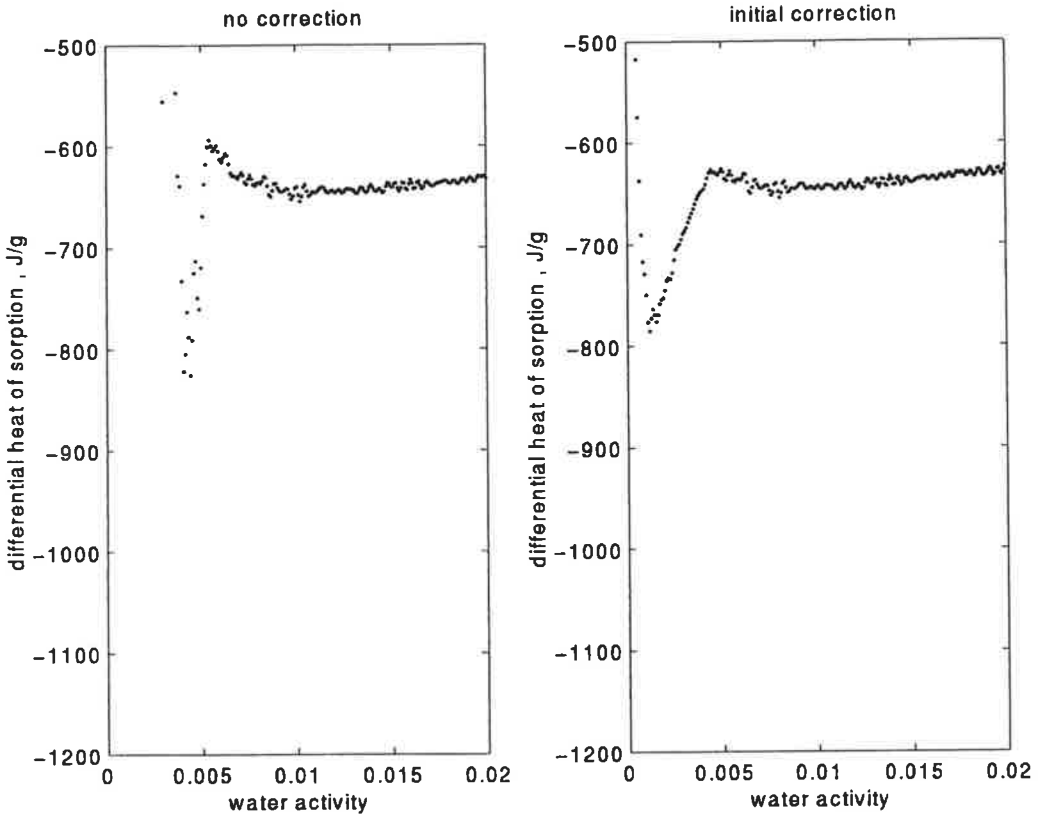

Figure 11: The evaluated heats of sorption from measurements with a CMC. The left diagram is without correction and the right diagram is with the correction applied.

10 Conclusions

The initial correction is a small, but important correction that always should be used. It will give values of both vapor activity and vapor concentration that are closer to the true values than the uncorrected values. The best correction procedure found is to use file 'incos4d2.mat' ('bestinco.m') for the first 300 s or for a shorter time if the user believes this is possible.

11 Acknowledgements

I thank Natalia Markova for helpful suggestions and for having run all the measurements I have used in this report. I also thank Nils and Dorthi Troedsson Research Foundation for support.

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13 Appendix A: Computer programs

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%tltest.m sorption time-lag test (a version of s4s.m)
%
%This program simulates measurements with SORP4 modelled as two
%capacity in the gas phase and one capacity for the sample
%
%                    Lars Wadsö 971029

%----------------input data & start data----------------
Dvh=2440; %heat of vaporization (J/g)
As=130e-6; %cross-section of sample (m2)
av=1;
a12=0;              %NOTE the units: in simulation cells: c (g)
a23=0;  %               isotherm: ciso (g/g)
as=0;   %              used in tltest: unew (g/g)
c12=0;
c23=0;
cs=0;
k1=9.0303e-007;
k2=k1;
k3=3.4747e-006;
C12=5.0122e-005;
C23=4.9597e-005;
%-------------------user input----------------------------
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=h*As*rho;
disp(' ');disp(['Sample mass = ',num2str(M*1e3),' mg']);
tend=input('end of simulation (s) :');if (tend==0)|(tend==[]);tend=48*3600;end
tout=input('time interval between outputs (s) :');if (tout==0)|(tout==[]);tout=5;end
isotype=input('type of isotherm ? (0=Dsh=0, 1=linear, 2=sigmoid, 3=hydrate, 4=low-high slope) :');
if (isotype<0)|(isotype==[]);isotype=1;end %standard case
if isotype==0 %conensation only
  aiso=[0 1];ciso=[0 0.3];hhhh=[0 0];
elseif isotype==1 %linear
  aiso=[0 1];ciso=[0 0.3];hhhh=[-1000 0];
elseif isotype==2 %sigmoid (wood Eucalyptys regnans, Christensen & Kelsey 1959)
  aiso=[0 0.05  0.10  0.40  0.70 0.80 0.90 0.95 1.00];
  ciso=[0 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 0]*(-4.18);
elseif isotype==3 %hydrate (Morphine sulphate)
  aiso=[0 0.029   0.031   0.229   0.231  0.95  1.0];
  ciso=[0 0.0001  0.0538  0.0539  0.135  0.136 0.2];
  hhhh=[0 -22 -22 -8 -8 7 8]*1e3/18;
elseif isotype==4 % low initial slope, crit. act. 0.5)
  aiso=[0 0.5 0.50001  1];
  ciso=[0 0.0001 0.00010001 0.3];
  hhhh=[0 0 -1000 0]*1e3/18;
end
xi=diff(ciso)./diff(aiso); %slope of isotherm
ix=diff(aiso)./diff(ciso); %inverse slope of isotherm
%--------------------simulation initialization------
dt=min([C12/(k1+k2) C23/(k2+k3) xi(1)*M/k3 5]);
t=0; %time in simulation (s)
cisomax=ciso(length(ciso)); %maximal possible activity
cisomaxend=0; %when cisomaxend=1 the simulation has to be stopped
toutnext=tout; %second output time (first is at t=0)
leg=1; %part on isotherm
out=1; %counter for outputs
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nout=ceil(tend/tout)+1; %approx. no of outputs
tt=zeros([1 nout]); %in tt the sim. time is saved
Pv=zeros([1 nout]); %in Pv the thermal power of vap. are saved
Ps=zeros([1 nout]);
tdisp=tend/10;
plusdisp=tend/10;
dtflag=0;
%--------------------simulation--------------------
tic
disp(['start dt=',num2str(dt),' s']);
while (t<tend)&(cisomaxend==0)
  t=t+dt; %increment time
  q1=k1*(av-a12);
  q2=k2*(a12-a23);
  q3=k3*(a23-as);
  unew=(cs+dt*q3)/M;
  if unew>cisomax;cisomaxend=1;disp('end of isot. reached');end
  if unew>ciso(leg+1); %entering new leg?
    dtflag=1;
    t=t-dt;
    dt=(ciso(leg+1)*M-cs)/q3;
    disp(['dt=',num2str(dt),' s at t=',num2str(t),' s']);
    t=t+dt;
    leg=leg+1;
  end
  c12=c12+dt*(q1-q2);
  c23=c23+dt*(q2-q3);
  cs=cs+dt*q3;
  a12=c12/C12;
  a23=c23/C23;
  as=interp1(ciso,aiso,cs/M);
  if toutnext<t %time for output?
    if tdisp<t
      tdisp=tdisp+plusdisp;
      disp(['t=',num2str(t/3600),' h with dt=',num2str(dt),' s (',num2str(t/tend*100),'%)']);
    end
    out=out+1; %index in output vectors
    tt(out)=t; %output time
    Pv(out)=q1*Dvh;
    Ps(out)=q3*(interp1(ciso,hhhh,cs)-Dvh);
    toutnext=toutnext+tout; %time for next output
  end
  if dtflag==1
    dt=min([C12/(k1+k2) C23/(k2+k3) xi(1)*M/k3 5]);
    disp(['dt=',num2str(dt),' s at t=',num2str(t),' s']);
    dtflag=0;
  end
end
%-----------------------cleaning up & interpolating-------------------
L=length(tt); %L=length of vectors
if out<L %clear the unused parts of Pv, Ps, tt
  Pv(out+1:L)=[];Ps(out+1:L)=[];tt(out+1:L)=[];
end
t=linspace(0,tout*(length(tt)-1),length(tt));
Pv=interpx(tt,Pv,t);
Ps=interpx(tt,Ps,t);
toc
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