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Some dynamic properties of a twin double microcalorimeter with a sorption cell

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Some dynamic properties of a twin double microcalorimeter with a sorption cell

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December 14, 1999

1 Introduction

We have designed a double twin microcalorimeter that simultaneously will measure the heat produced in two parts of a vessel situated approx. 70 mm from each other. Figure 1 shows a drawing of the instrument. The double twin microcalorimeter has been designed to fit into the 2277 TAM ampoule calorimetric unit of Thermometric AB (Järfälla, Sweden). The two calorimeters of the double twin calorimeter are therefore housed in the same type of steel can as one twin 2277-000 20 ml ampoule microcalorimeter. This has been made possible by the use of smaller heat sinks and a thermally designed heat flow breaker between the two twin calorimeters so that they will not disturb each other.

The heat flow breaker between the calorimeters is insulated from the two calorimeters. At the same time it has more contact with the thermostated bath than the calorimeters so the major part of a heat leak from one calorimeter towards the other will flow out into the bath instead of disturbing the other calorimeter.

In a double twin calorimeter the properties of the instrument will be dependent on the measurement vessel used. The properties of the instrument will therefore be described with the sorption vessel that is schematically shown in Fig. 2. The top part of the vessel is positioned in the top calorimeter and the bottom part is positioned in the bottom calorimeter. The top and bottom parts of the vessel are connected by a 9 mm diameter tube with a low thermal conductance as it is made of 0.1 mm stainless steel. On the middle

of the tube is a heat exchanger that connects to the heat flow breaker. When in use in the calorimeter a copy of the vessel is placed in the reference.

Figure 3 shows the heat transfer model used to optimize the design of the calorimeter. Each circle is a heat capacity in the calorimeter and each line denotes a heat conductance between heat capacities. This type of model is realistic for a microcalorimeter that consists of different blocks of aluminum with very good thermal conductivity separated by air gaps and heat flow sensors with relatively low thermal conductivity. The heat capacities were calculated as the sum of the heat capacities of the parts, e.g. C_4 is the sum of the heat capacity of the top part of the sorption vessel, the ampoule holder, and half the thermocouple plate. The thermal conductances were estimated by connecting the relevant parts in series and parallel, e.g. k_{12} is the thermal conductances of two steel screws and two plastic distances, all in parallel. Data on the thermocouple plates were from the manufacturer (Melcor). It should be noted that the heat capacities are easy to calculate rather accurately, but the thermal conductances are much more difficult to assess and will therefore have quite large uncertainties. However, the model presented is good enough to show the principles of the instrument and give results close to those found from measurements.

The model has been solved for different cases with a forward difference program written in MATLAB. Some results are given in the sections below. The methods used may be found in modern text-books on heat transfer.

2 Cross-talk

One obvious problem of placing two calorimeters very close to each other is that the heat produced in one calorimeter will somehow also flow to the other calorimeter and may also give a signal from that other calorimeter. In our earlier designs the cross-talk was nearly one percent and one main aim with the design of the present instrument was to lower this value.

The cross-talk is defined as the ratio of what is measured in calorimeters 1 and 2, when the thermal power is only produced in calorimeter 1. Its numerical value depends to some extent on how it is defined. We have used the following method (definition) to assess the cross-talk: *A 1200 s thermal power pulse is applied in calorimeter 1. The cross-talk is the maximal thermal power measured in calorimeter 2 divided by the maximal thermal power measured in calorimeter 1.*

When we measured the cross-talk in the double twin calorimeter with the sorption vessel we found that it was approx. 0.04% and 0.06% for top-to-bottom and bottom-to-top, respectively.

3 Cross-talk in a perfectly balanced calorimeter

First I have made a simulation with a perfectly balanced calorimeter. Figures 4-7 show the result of a simulation with a 1200 s 100 μ W pulse in the top calorimeter and then a similar pulse in the bottom calorimeter. The whole simulation lasted for 16000 s. The cross-talks calculated from the simulations were as follows:

$$\begin{array}{ll} \text{top to bottom} & 3 \cdot 10^{-6} \\ \text{bottom to top} & 3 \cdot 10^{-6} \end{array}$$

4 Cross-talk in a unbalanced calorimeter

Secondly I have made a simulation with an unbalanced balanced calorimeter by increasing C_4 by 5%. Figures 8-11 show the result of these simulation with a 1200 s 100 μ W pulse in the top calorimeter and then a similar pulse in the bottom calorimeter. The whole simulation lasted for 16000 s. The cross-talks calculated from the simulations were as follows:

$$\begin{array}{ll} \text{top to bottom} & 3 \cdot 10^{-6} \\ \text{bottom to top} & 81 \cdot 10^{-6} \end{array}$$

From the simulations with a perfectly balanced calorimeter and an unbalanced calorimeter one sees that the cross-talk is very much dependent on how well balanced the calorimeter is. This can be explained as follows. There is a very low cross-talk in the balanced calorimeter because the heat that flows from one part of the calorimeter to the other, e.g. from top to bottom, does so mainly through the heat sinks and the heat flow breaker and thus influences both sides of the calorimeter in exactly the same way. The very low cross-talk measured comes from the heat flow through the thin stainless steel tubes of the calorimetric vessel. During a period of heat production heat will flow to all parts of the double twin calorimeter as the temperature

will have to increase in the whole calorimeter (one of the functioning of the references is to take away the influence of this temperature change in the whole calorimeter). In the perfectly balanced double twin calorimeter the cross-talk is therefore the difference between two relatively large, but nearly equal, numbers.

In the unbalanced double twin calorimeter the inequality of the two sides of the calorimeter makes the differential connection of the calorimeter not so good. The heat flows and temperature increases may be very similar, but twin arrangement is not perfect. The resulting cross-talk will be like the difference between two relatively large, but not as nearly equal, numbers. An important conclusion that may be drawn is that it is very important to balance a double twin calorimeter carefully.

A somewhat similar situation exists in a normal twin arrangement, but here the correction made by the twin is in many cases rather large and if this correction is 5-10% in error the final error will not be so large. It is like taking the difference of two quite different numbers; the difference will not change much if there is a small change in one of the numbers.

5 Monto Carlo simulation of cross-talk

I have run the simulation model of the double twin calorimeter 5000 times with different imbalances. The reference parts and the central parts were left unchanged (i.e. as a reference), but unbalances were introduced on the sample side by assigning normally distributed errors as follows (parameter and standard deviation):

C_4	5%
C_5	5%
C_6	5%
k_{14}	10%
k_{25}	10%
k_{36}	10%
k_{45}	10%
k_{40}	10%
k_{56}	10%

Note that the Seebeck coefficients were not randomly distributed.

Figure 12 shows the result of the simulations. The three vertical lines in each plot are \pm the standard deviation and the mean. It is seen that the cross-talk is in most cases is less than 0.03% for the cases tested. It is difficult to know how unbalanced a calorimeter is, but the above values are probably quite good guesses for the heat capacities. For the thermal conductances, however, the values are probably in many cases on the low side as thermal conductances may be greatly influenced by small changes in different parameters (e.g. contact resistances).

6 Steady-state heat flows

I have also made a long term simulation with constant thermal powers in the double twin calorimeter. A thermal power of $100 \mu\text{W}$ was applied in the top sample heat capacity (C_4) for 16000 s. Figures 13-16 shows the result. Note how the heat mainly flows from the sample C_4 to C_1 and further to the reference C_7 . From the top heat sink C_1 the heat flows both to the thermostated environment and to the heat flow breaker C_2 . From the heat flow breaker C_2 the heat flows both the thermostated environment and to the bottom heat sink C_3 .

The simulation shows that there are quite large heat flows within the whole calorimeter and that the top and the bottom are not very well separated from each other. The instrument only works because it is well balanced. One could decrease thermal conductances k_{12} and k_{23} to decrease the heat flow between the top and the bottom through the heat flow breaker. However, this would result in higher temperature differences between C_4 and C_6 , and possibly to higher heat flows through k_{45} and k_{56} which would very much increase the cross-talk.

7 Conclusions

The following conclusions have been drawn from the simulations:

- The measured cross-talk (0.04 and 0.06%) is in reasonable agreement with the cross-talk from the simulations..
- It is very important to balance a double twin calorimeter to decrease the influence of the cross-talk.

- There are quite high thermal conductance paths between the top and the bottom, but these are probably beneficial to the double twin arrangement as one would otherwise risk higher heat flows directly between top and bottom parts of the vessel (ampoules).
- It is important that the top and bottom parts of the calorimetric vessel (ampoules) have low thermal contact with each other.

Figure 1 The double twin microcalorimeter.

Figure 2 The sorption vessel.

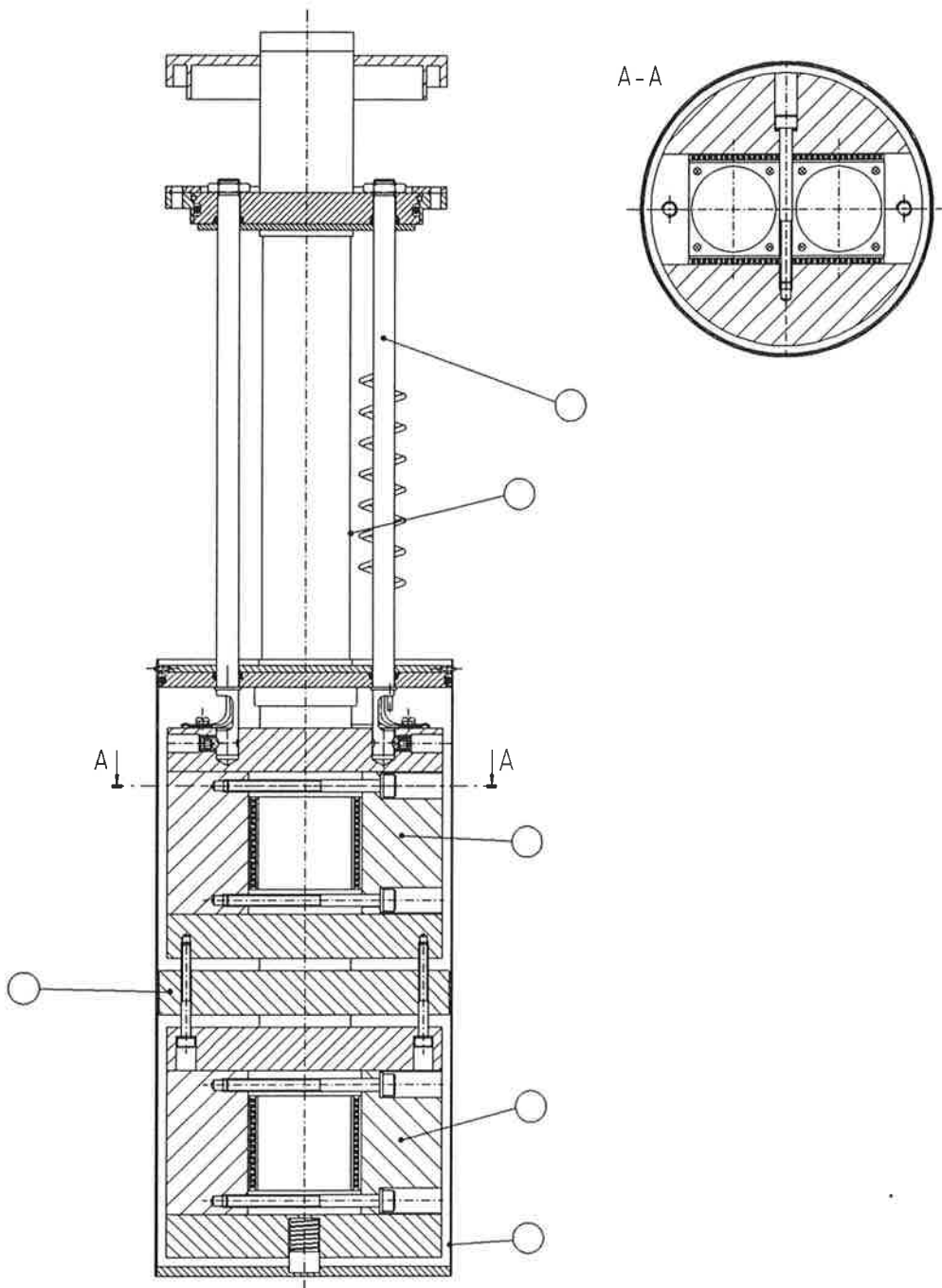
Figure 3 The thermal model of the double twin microcalorimeter with the sorption vessel. Circles are heat capacities (area proportional to heat capacity) and lines are thermal conductances (thicknesses of lines proportional to conductances). Lines angled down-right are thermal conductances to the thermostated environment. 1. Top heat sink. 2. Heat flow breaker. 3. Bottom heat sink. 4. Top sample ampoule part. 5. Sample side heat exchanger. 6. Bottom sample ampoule part. 7. Top reference ampoule part. 8. Reference side heat exchanger. 9. Bottom reference ampoule part.

Figure 4-7 Results from simulation of cross-talk in balanced calorimeter.

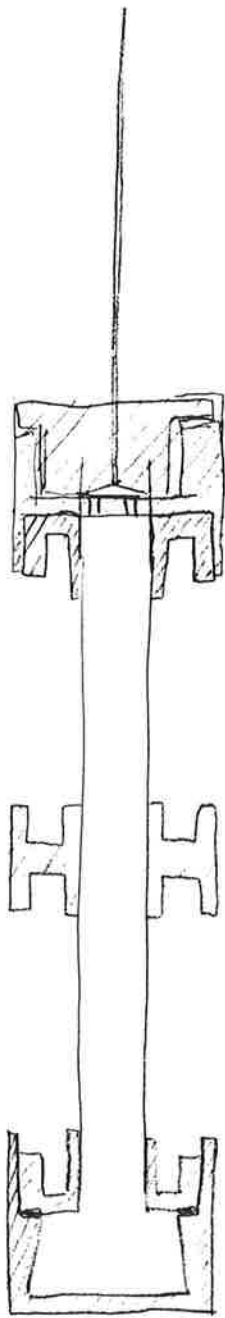
Figure 8-11 Results from simulation of cross-talk in unbalanced calorimeter.

Figure 12 Results from Monte Carlo simulations of cross-talk.

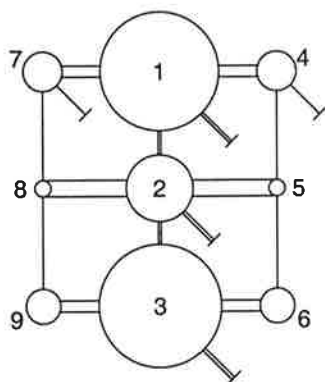
Figure 13-16 Results from simulation with constant thermal power in the top sample ampoule.



Figur 1



Figur 2



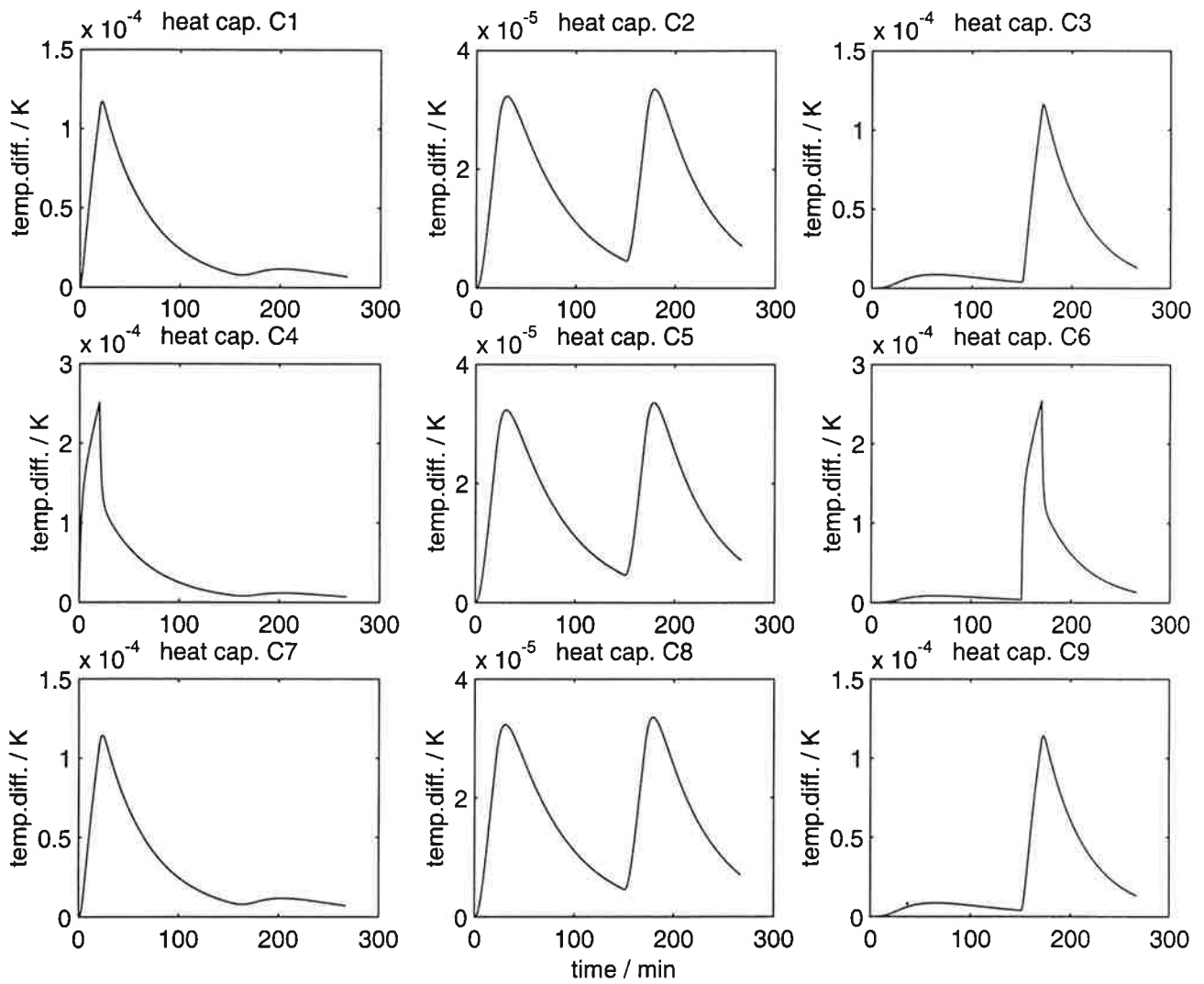
Heat capacities

$C_1=642 \text{ J/K}$
 $C_2=202 \text{ J/K}$
 $C_3=683 \text{ J/K}$
 $C_4=71 \text{ J/K}$
 $C_5=12 \text{ J/K}$
 $C_6=55 \text{ J/K}$
 $C_7=71 \text{ J/K}$
 $C_8=12 \text{ J/K}$
 $C_9=55 \text{ J/K}$

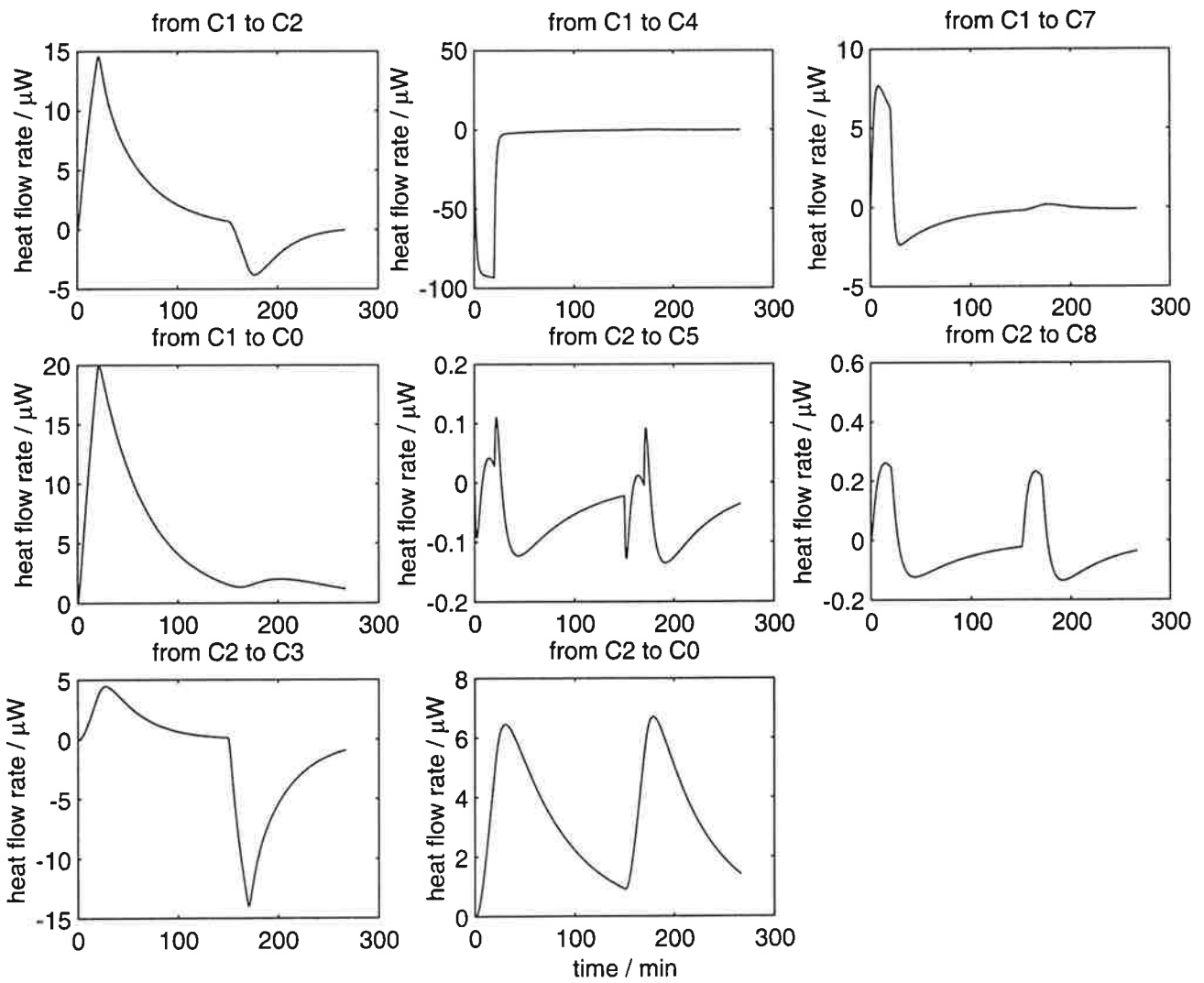
Thermal conductances

$k_{12}=0.16 \text{ W/K}$ $k_{39}=0.68 \text{ W/K}$
 $k_{14}=0.68 \text{ W/K}$ $k_{30}=0.22 \text{ W/K}$
 $k_{17}=0.68 \text{ W/K}$ $k_{45}=0.0015 \text{ W/K}$
 $k_{10}=0.17 \text{ W/K}$ $k_{40}=0.0007 \text{ W/K}$
 $k_{23}=0.16 \text{ W/K}$ $k_{56}=0.0015 \text{ W/K}$
 $k_{25}=1 \text{ W/K}$ $k_{78}=0.0015 \text{ W/K}$
 $k_{28}=1 \text{ W/K}$ $k_{70}=0.0007 \text{ W/K}$
 $k_{20}=0.2 \text{ W/K}$ $k_{89}=0.0015 \text{ W/K}$
 $k_{36}=0.68 \text{ W/K}$

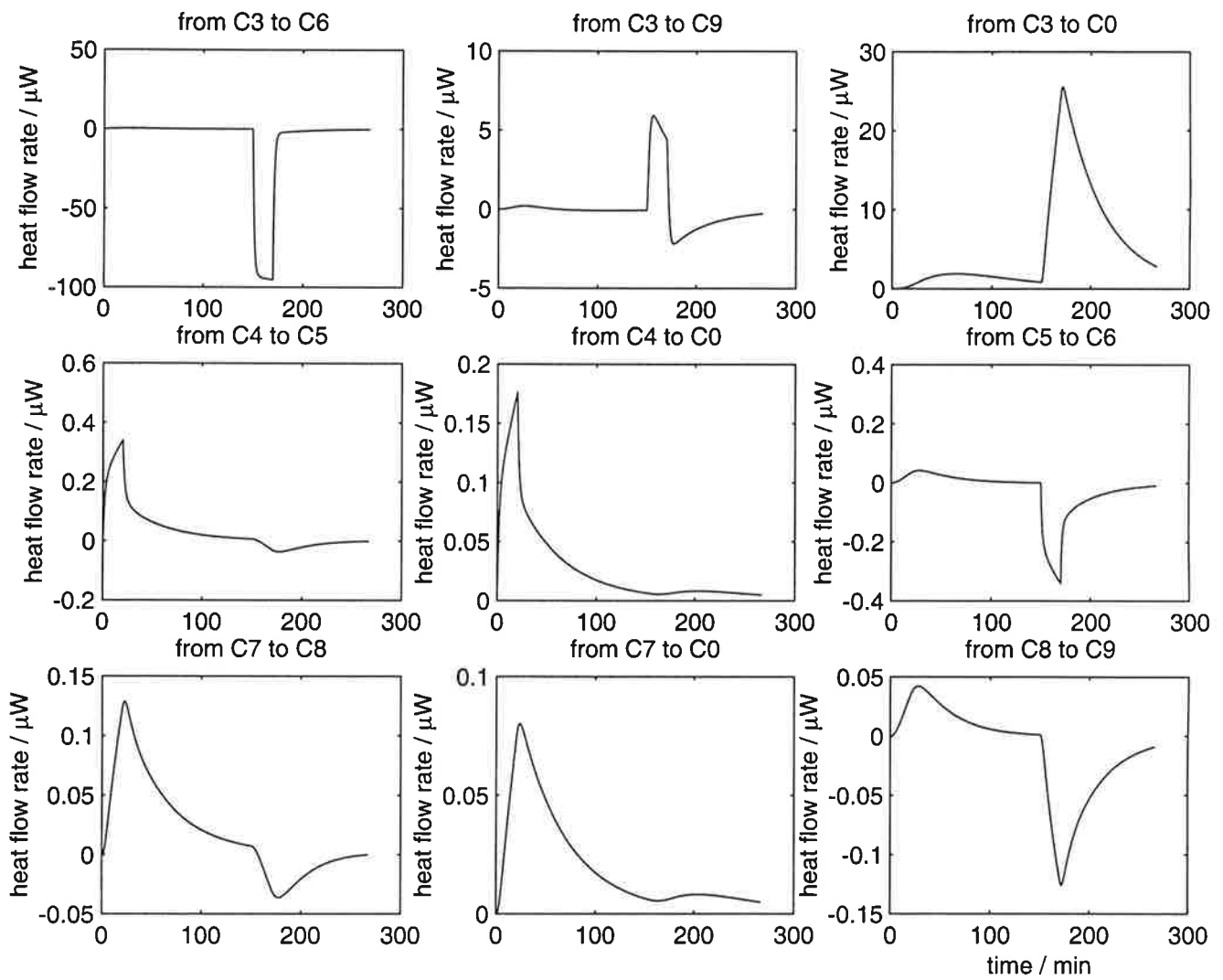
Figur 3



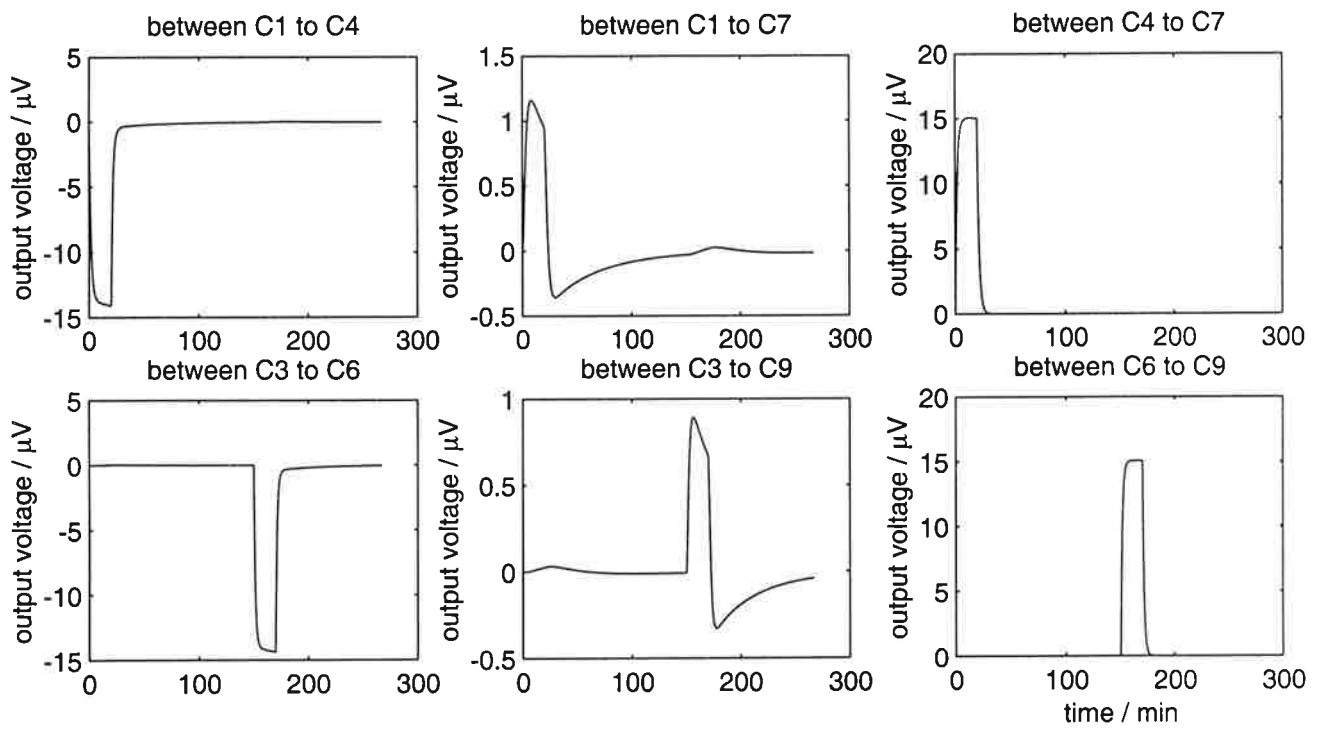
Figur 4



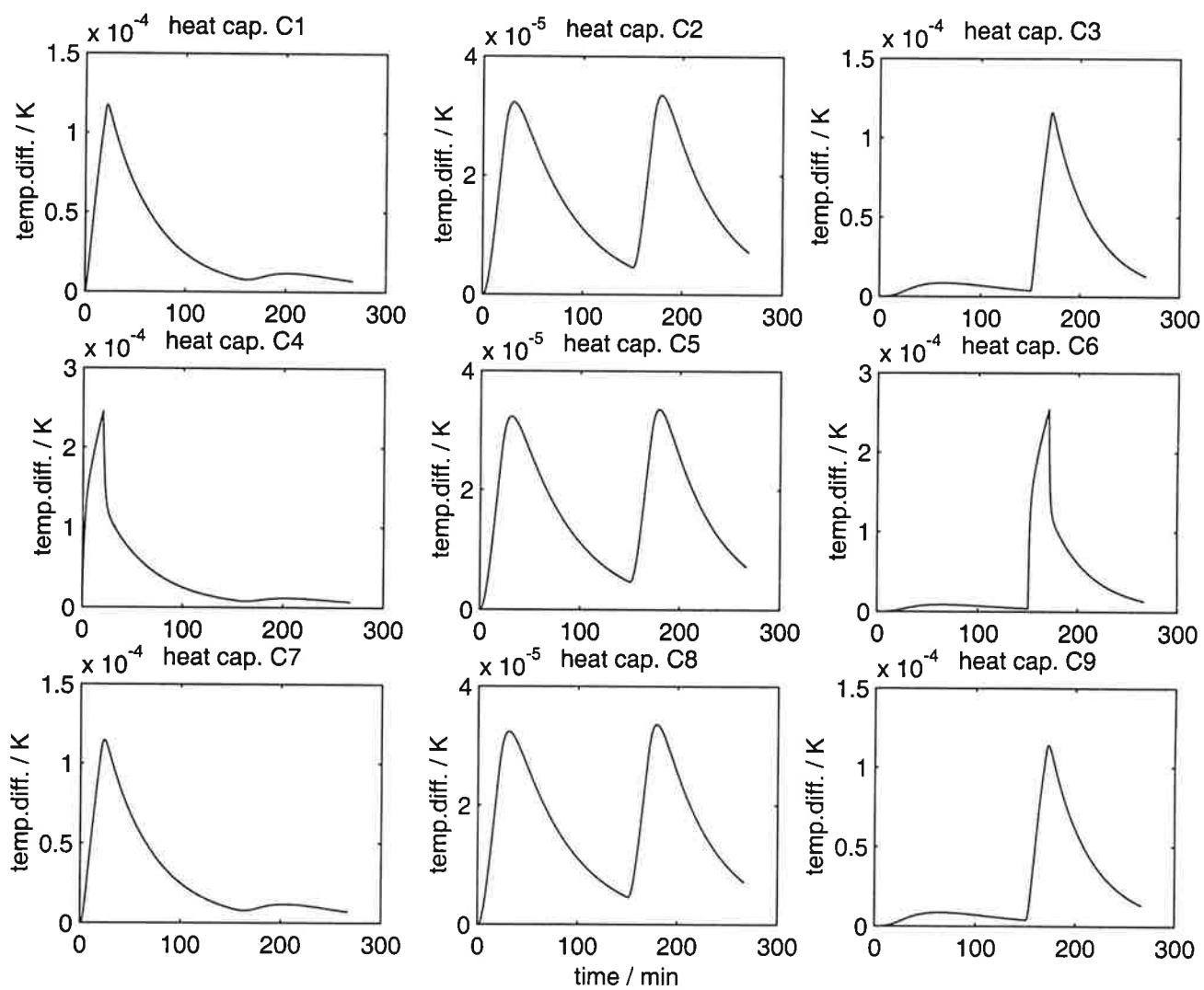
Figur 5



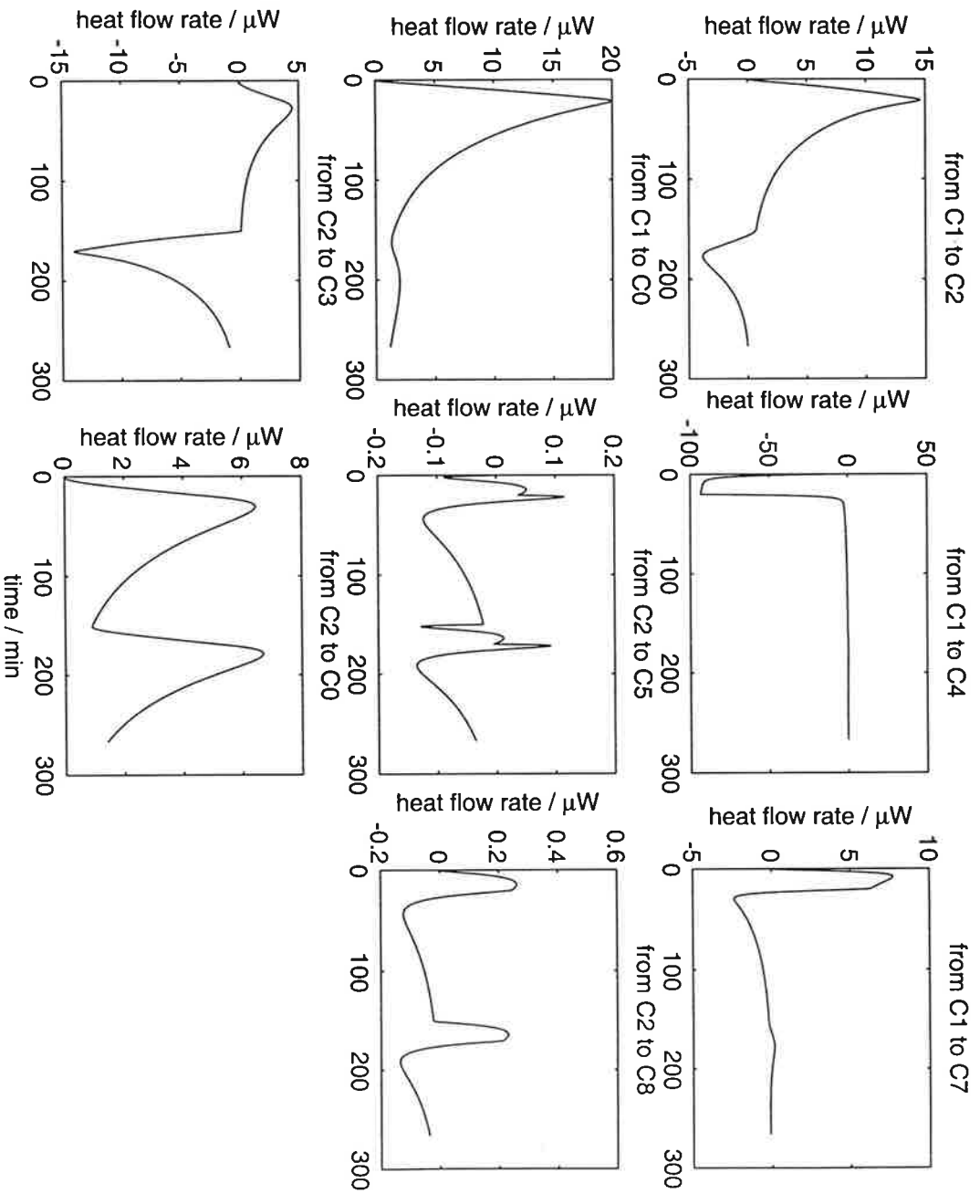
Figur 6



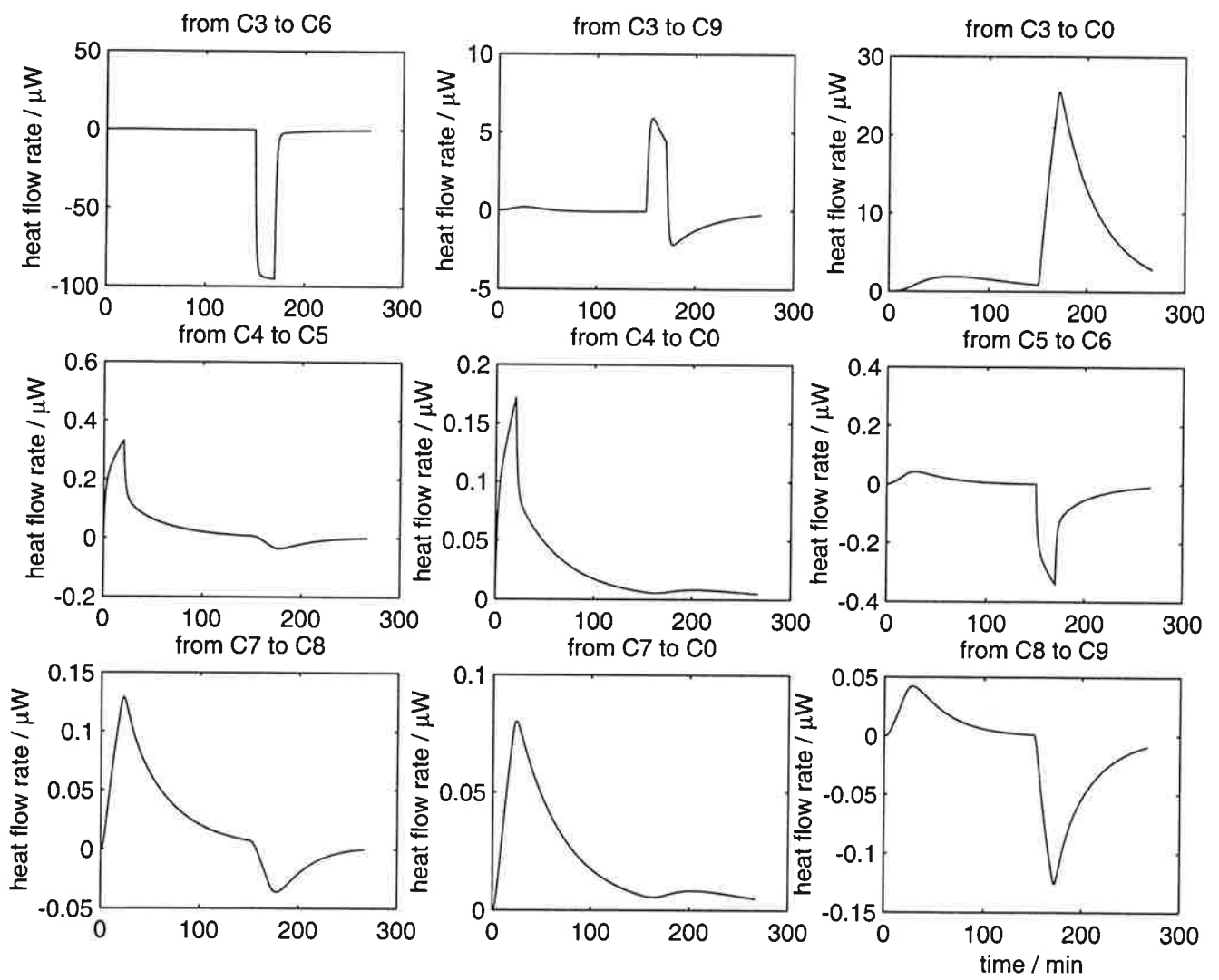
Figur 7



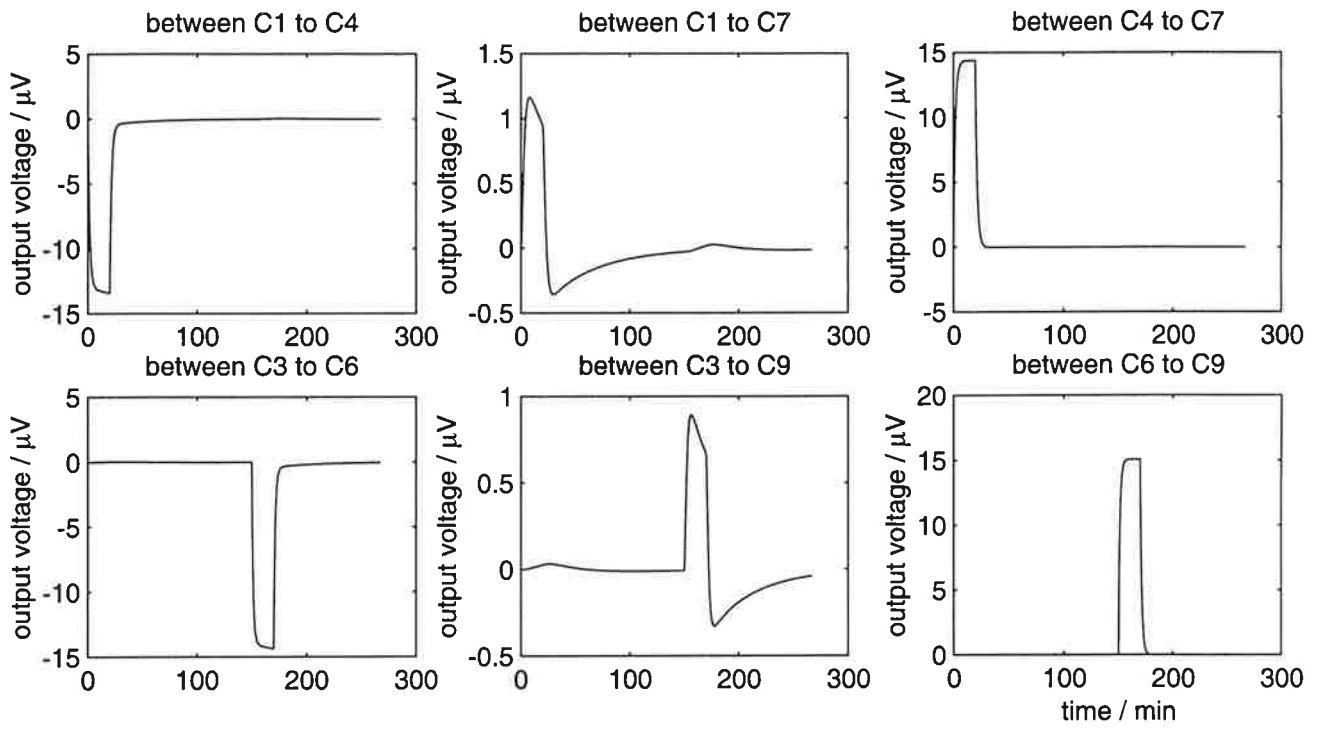
Figur 8



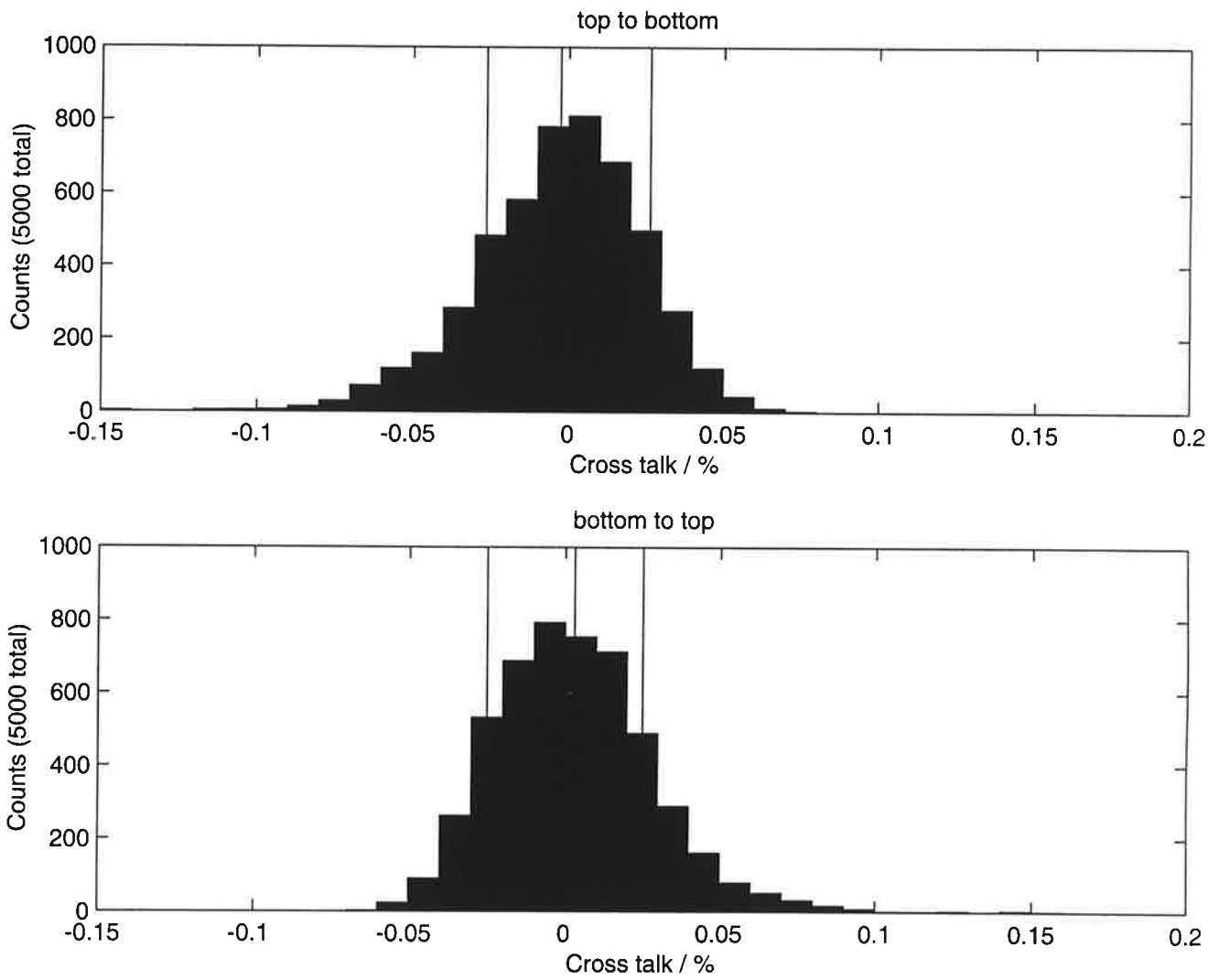
Figur 9



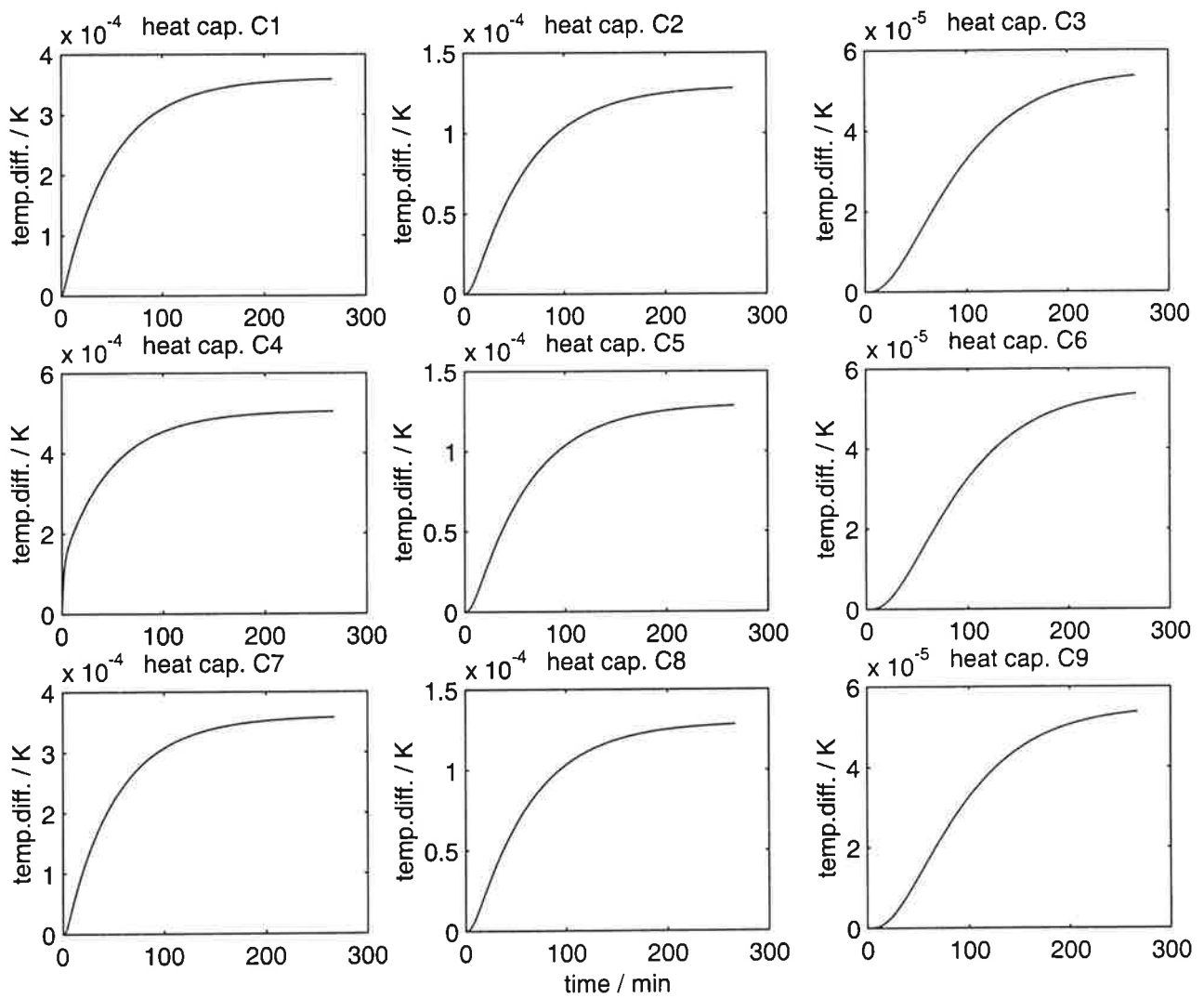
Figur 10



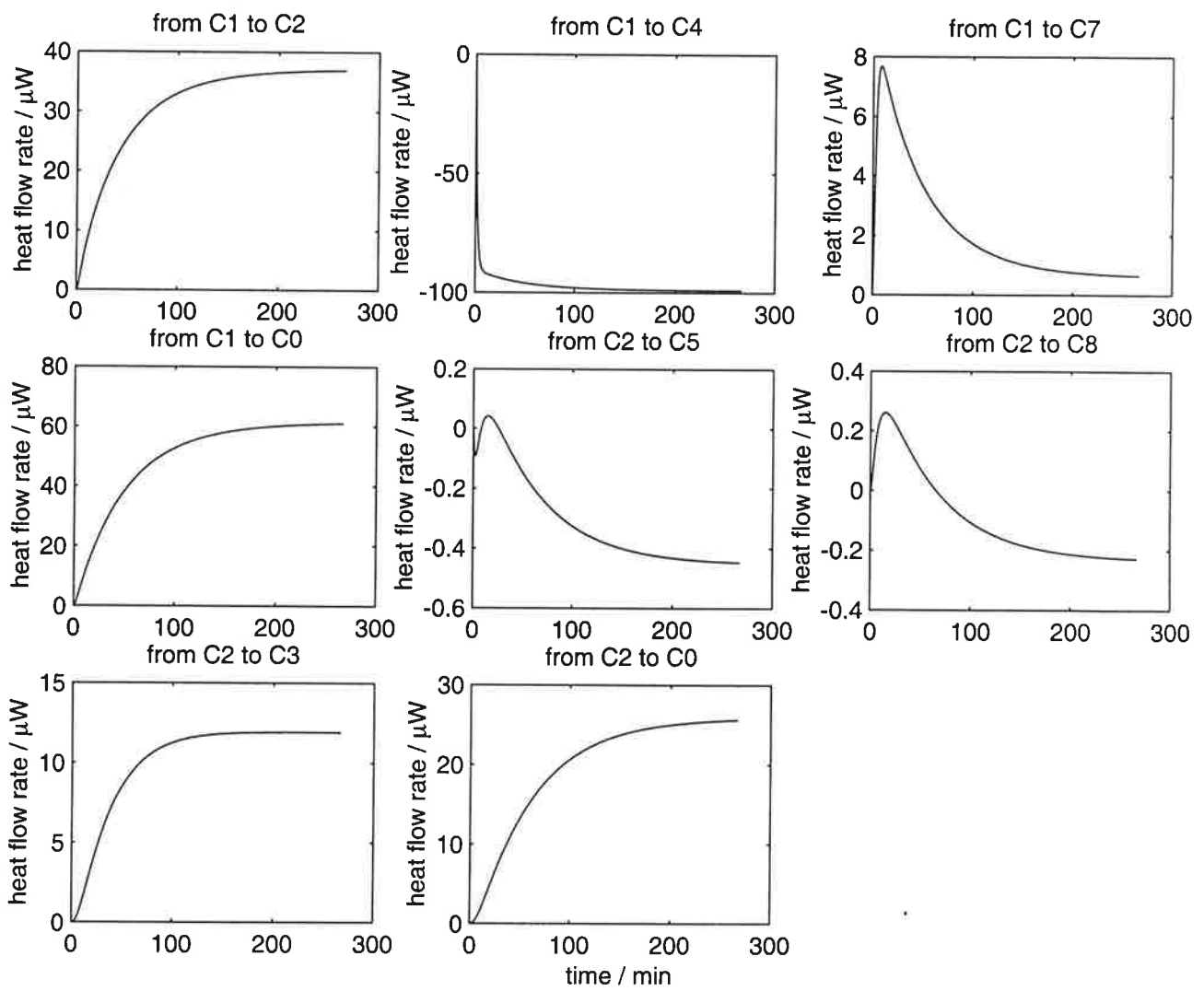
Figur 11



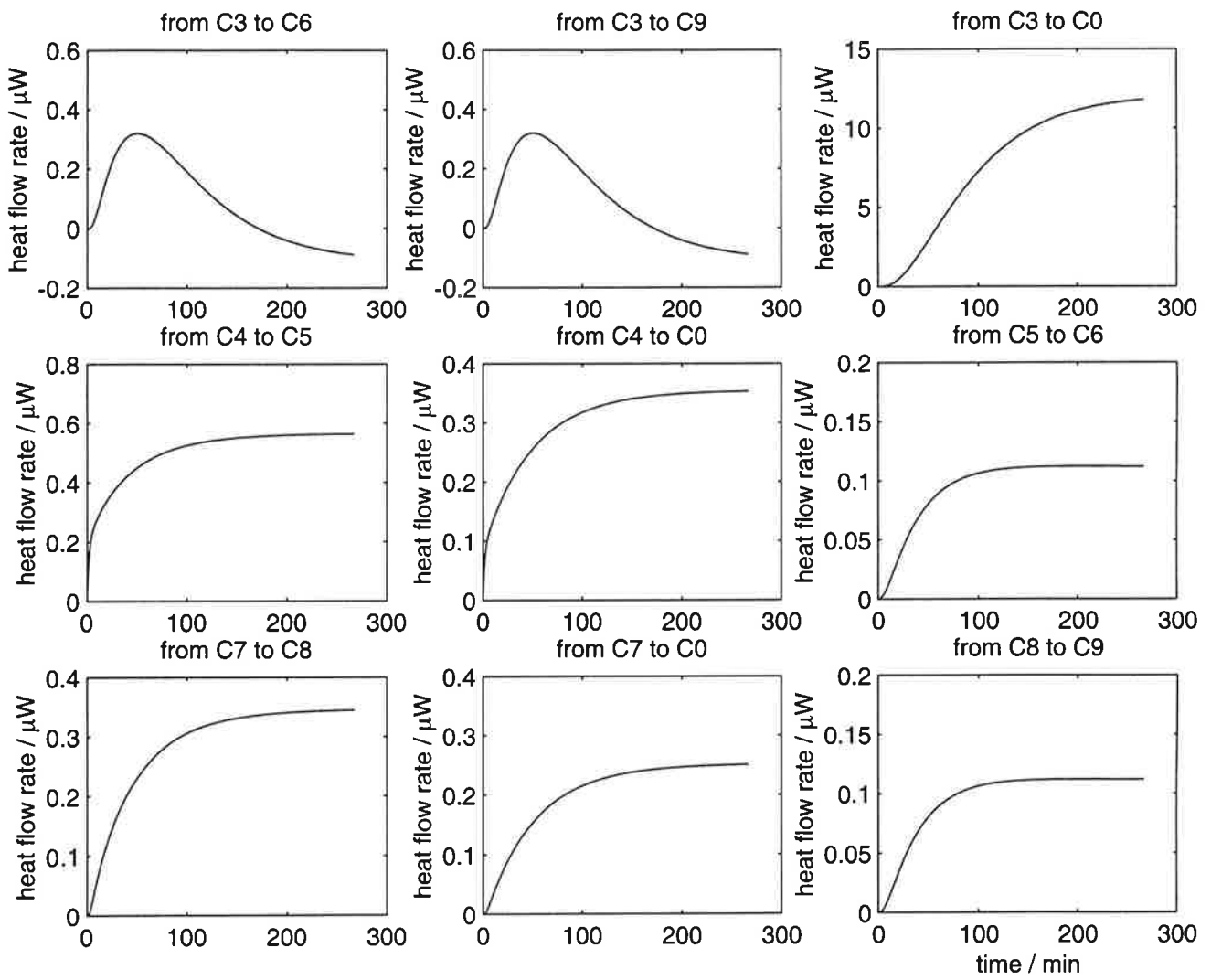
Figur 12



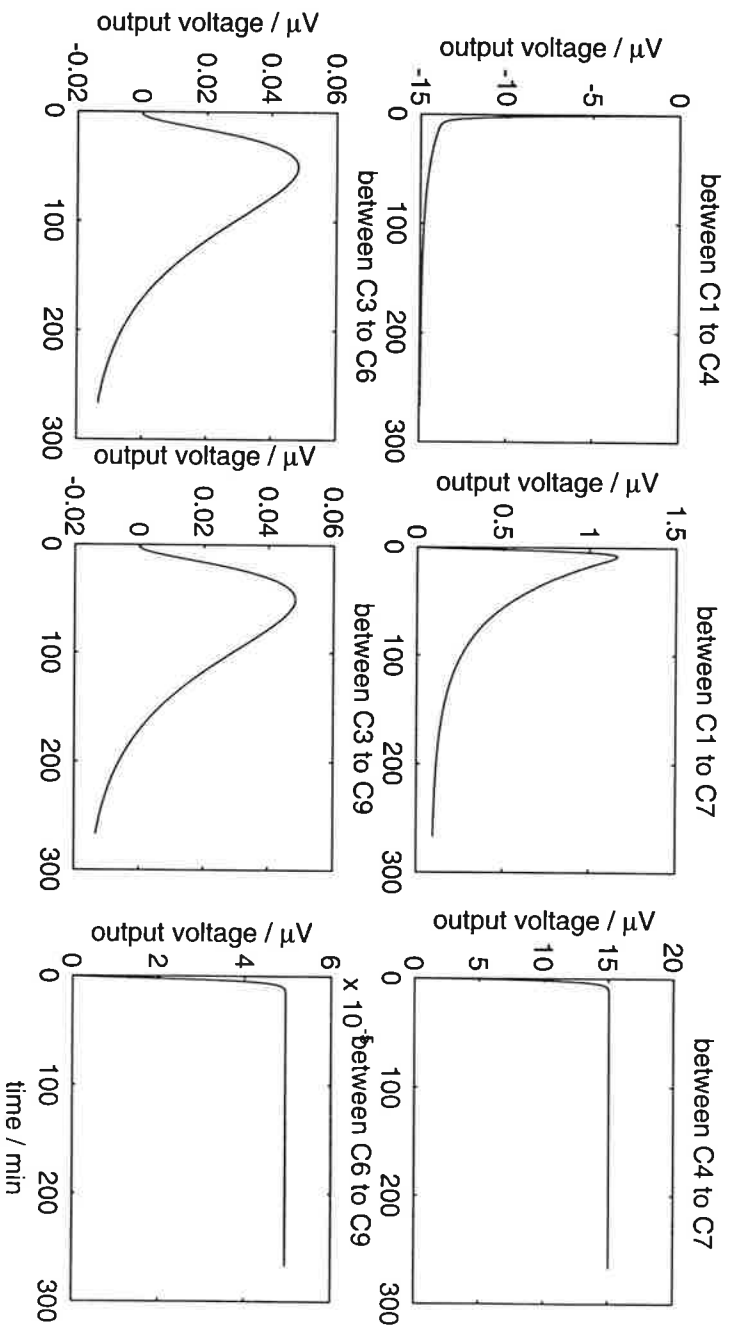
Figur 13



Figur 14



Figur 15



Figur 16

