Calibration and balance of reference

Two types of calibrations

- Heat flow calibration – for ‘slow’ processes
- Dynamic calibration - for ‘fast’ processes

Thermal inertia ⇔ Time delay

- Due to the thermal inertia of a calorimetric unit the true response in heat flow by a sample will differ somewhat from the heat flow monitored by the heat detectors)
- For fast processes, i.e. response time < 10-15min dynamic calibration should be used to give true process rates

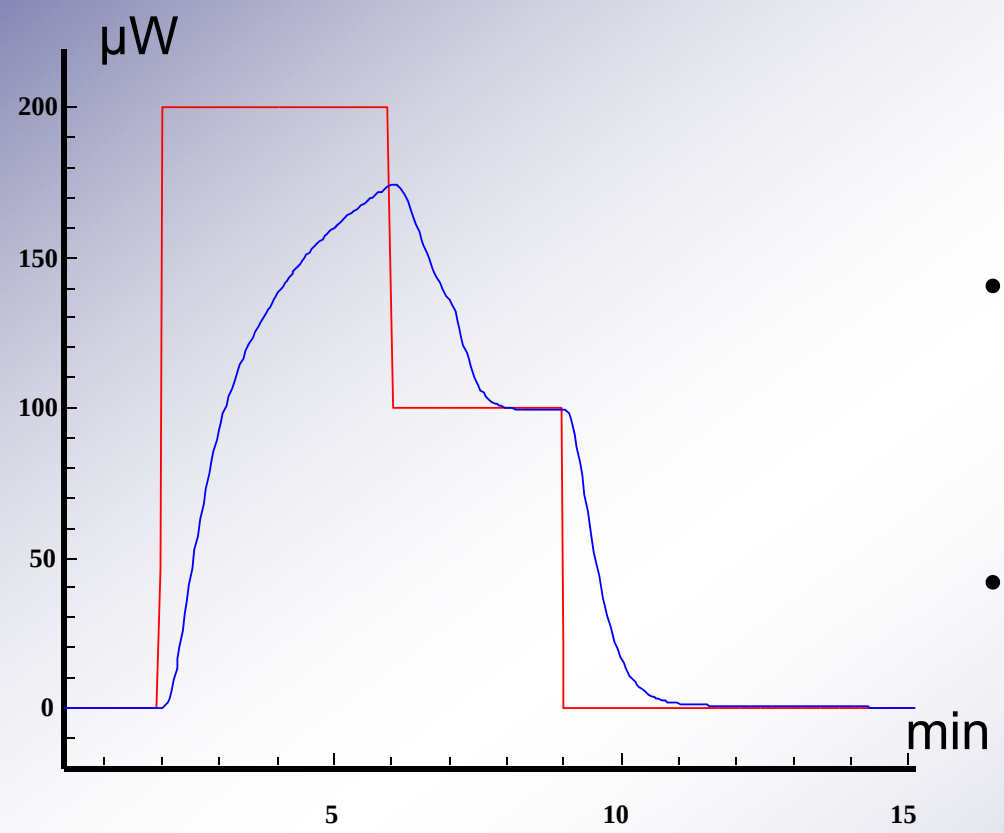
Dynamic correction

For reactions where the slope of the heat flow time curve (ϕ) is changing rapidly a dynamic correction can be applied to obtain the true response of the sample (P) using the following formula (*Tian's equation*) ;

$$P = \phi + \tau \frac{\mathrm{d}\phi}{\mathrm{d}t}$$

τ = a time constant obtained from dynamic calibration

Dynamic Calibration



- Dynamic calibration refer to calibration under non-steady state conditions, i.e. during a curvature of the heat flow signal
- A known electrical calibration power is applied in two steps and the dynamics of the curvature is analysed in terms of time constants.
- A dynamic calibration might be needed if the response time of a process is less than 15 min since the shape during that part will be affected

Dynamic Correction function in TAM Assistant

- The TAM Assistant software contains functions for considering the effects of the thermal inertia, *i.e*. it calculates a property close to the true heat production rate in the sample.
- TAM Assistant uses *two* time constants rather than one to get a better precision in the correction (*cf*. Taylor expansion). In this case the fitting parameters has no relevant physical interpretation

Effect of Dynamic calibration

- **Heat flow data** will not reflect the true response of the sample for reactions with response times less than 10 min.
- **Dynamically corrected data** represents the true data of the sample and has been calculated from Heat flow data using the information about time constants obtained from Dynamic calibration.

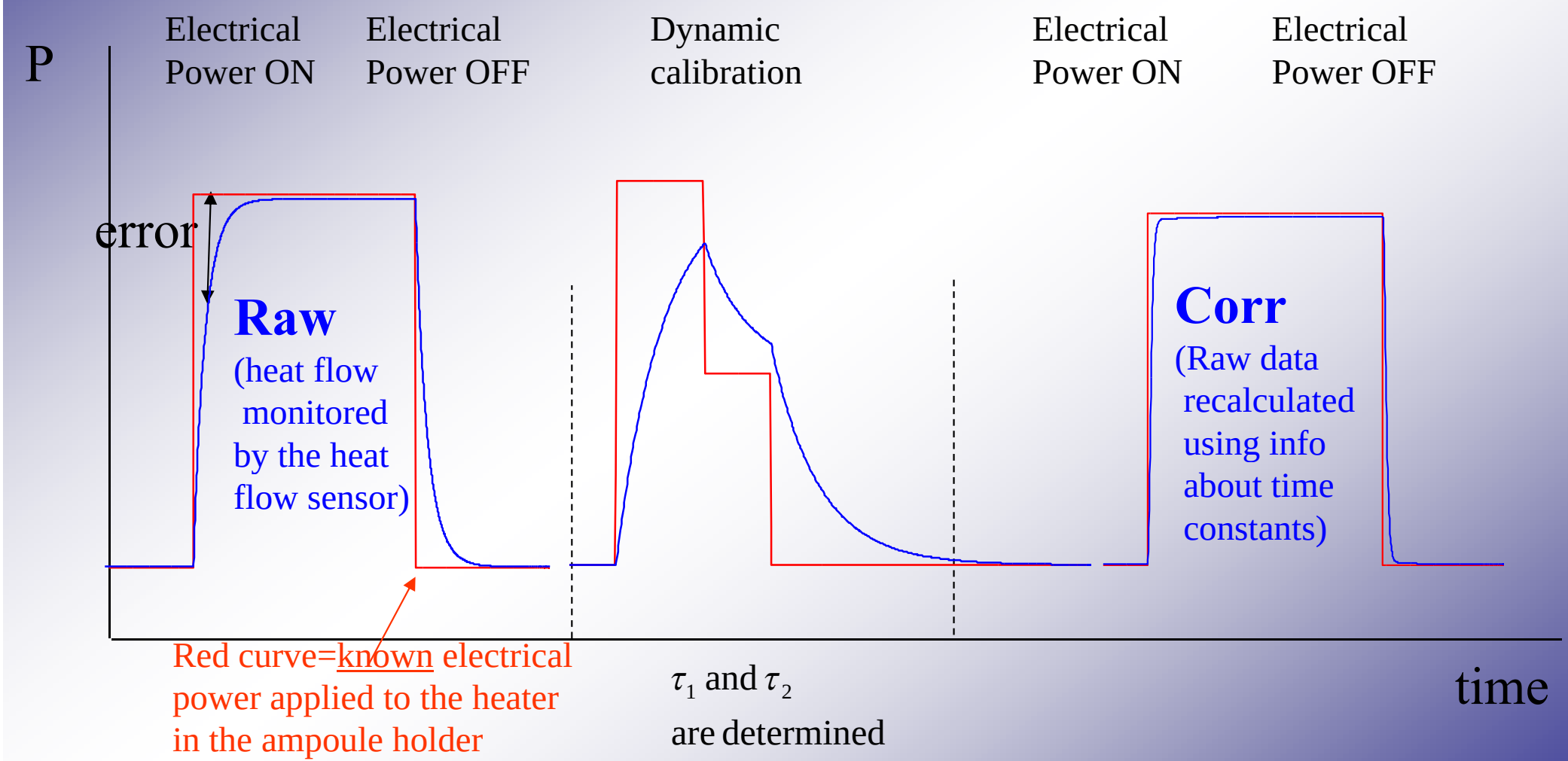
$$P = \phi + (\tau_1 + \tau_2)\frac{d\phi}{dt} + \tau_1 \cdot \tau_2 \frac{d^2\phi}{dt^2}$$

Heat flow and “corrected” data

- If only a static calibration has been performed only heat flow data, ϕ, (data monitored by the heat detector) can be displayed

- If a dynamic calibration has been performed, dynamically corrected data, i.e. data close to the true response of the sample, is displayed

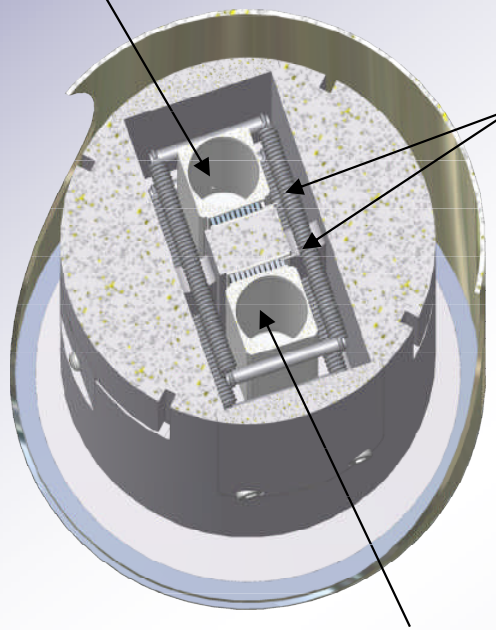
Heat flow and corrected data



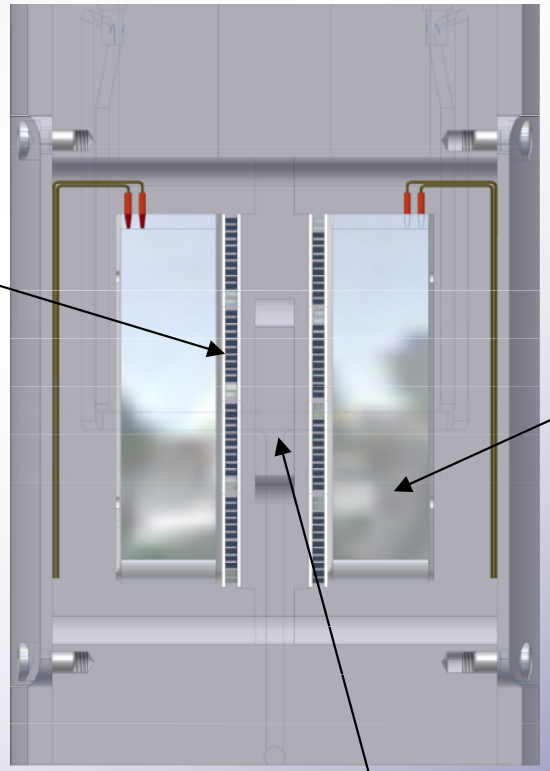
The 3201 Nanocalorimeter

Sample Ampoule holder

Twin System



Thermoelectric Modules (Seebeck modules)



Foil Heaters for Calibration

Reference Ampoule holder

Heat Sink Partition wall

Calibration conditions

- **Titration ampoules experiments**
  - the titration ampoule loaded with the solution should be in measuring position to consider heat loss effects through the ampoule
  - a reference ampoule should be in position
  - stirrer should be on

Dynamic Calibration

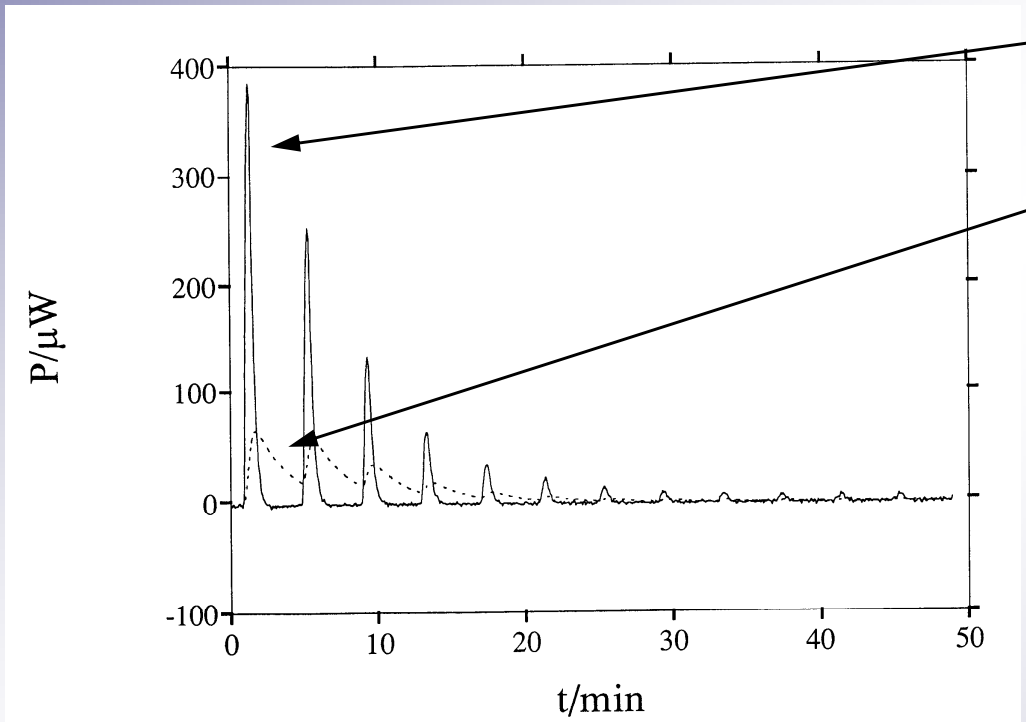
-General procedure

- Set measuring principle to “Dynamic correction” (Calorimeter device / control / measuring mode.
- Introduce the ampoule with sample (or a sample “mimic”).
- Wait until the calorimetric signal is stable.
- Start the calibration: there are two options i) time-constant calibration and ii) full dynamic calibration (Calorimeter device / control / perform calibration ..)
- After 20-30 minutes, the dynamic calibration is completed and the calibration heater is turned off automatically

A new calibration should be performed

- Heat flow and dynamic calibration when:
  - New ampoule type is used
  - Referred to as “Full dynamic calibration” in the software”
- Dynamic calibration when
  - Sample volume is changed
  - Solvent is changed
  - Stirring rate significantly changed
  - Referred to as “Time constant calibration” in the software

Dynamic calibration



Corrected signal

Raw (heat flow) signal

$$P = \phi + (\tau_1 + \tau_2)\frac{d\phi}{dt} + \tau_1 \cdot \tau_2 \frac{d^2\phi}{dt^2}$$

Choice of Reference Materials

- A reference material is used to balance the heat capacity of the sample and the reference ampoule.
- With a good balance in heat capacity the short-term noise will be reduced. However, if the system is not well-balanced the average heat flow values is not affected.
- A proper balancing of the ampoules is needed when the response in heat flow is low, e.g. during titration experiments.
- Example of reference materials: sand, glass pearls, water

Balancing sample and reference

- Calculate from heat capacity
- Calculate from time contants
  - Measure τ of an empty ampoule
  - Measure τ of ampoule with different amount of *e.g.* water

END