

Decomposition Kinetics with Heat Flow Calorimetry & Pressure Measurements

Exemplified by the Degradation of Sodium Percarbonate

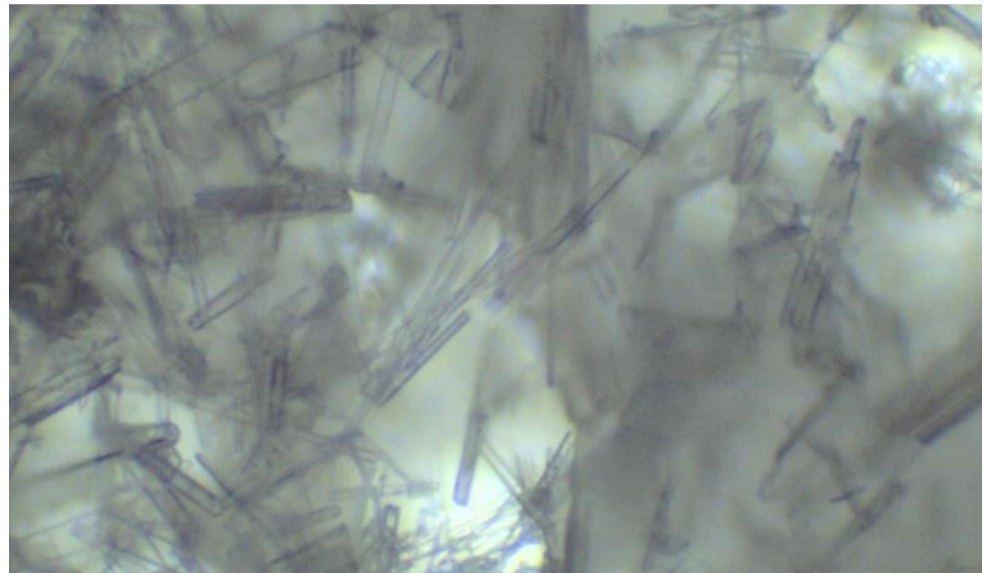
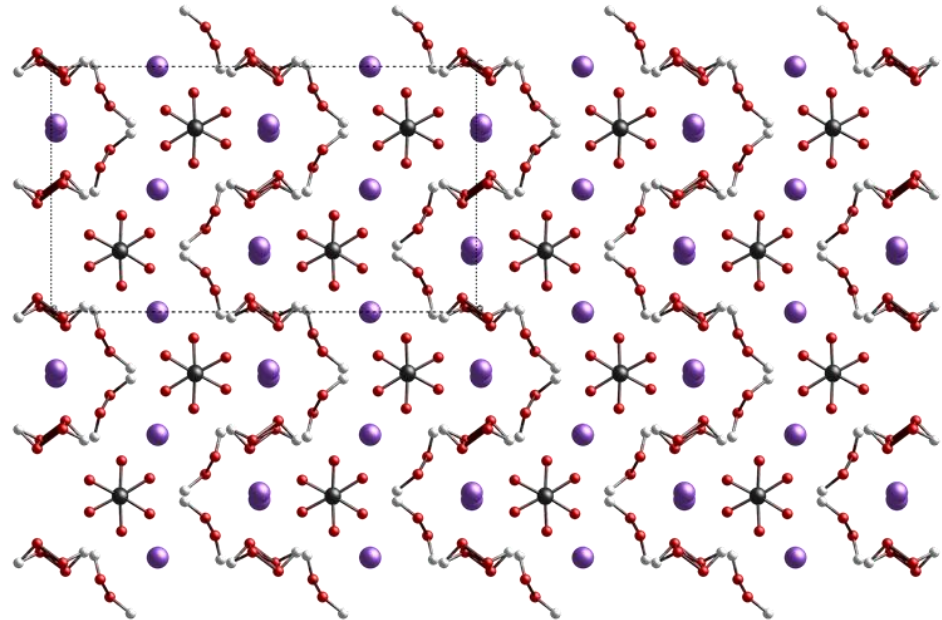
TA User meeting @ the National Space Center

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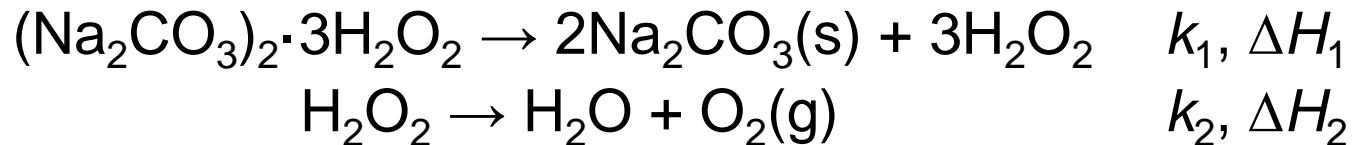
Sodium Percarbonate

- Sodium percarbonate, SPC, is an adduct of sodium carbonate and hydrogen peroxide – $\text{Na}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}_2$.
- At ambient conditions, SPC crystals has elongated, needle like shapes with the crystallographic structure of the orthorhombic system.
- SPC is a typical ingredient in tableted, compacted , and powder detergents to deliver hydrogen peroxide to the wash solution where is functions bleaching agent.
- An estimated 300,000-500,000 tonnes is produced world-wide annually at some 20-30 production sites.



On the degradation of SPC

- In the solid state SPC degrades spontaneously according to the following simplified scheme:



- The reaction is exothermic with an overall enthalpy change, ΔH_{1+2} , of approximately 600 J g^{-1} or 95 kJ mol^{-1} (as measured in this work).
- The kinetics of the degradation is fairly complex in a closed environment, where temperature plays a role as well as the amount of water present in the system.
- The development of a product surface layer around the particles during the degradation influences the reaction rate.

Current analysis of safe storage

The spontaneous decomposition of SPC results in self-heating while stored.

If not stored properly runaway reactions may occur with explosion and personal injury (*cf.* Unilever).

Two of the worlds largest producers of laundry detergents, Unilever and P&G, has developed a method for the assesment of safe storage conditions of SPC.

Samples are measured in an isothermal microcalorimeter and the heat flow value at two points in time, 16 and 48 hours, are taken and fed into a heat balance model that simulates the temperature evolution in time and space in a storage container.

Popov, Muravlyansdsky and Phipps. TA Application note 22034.

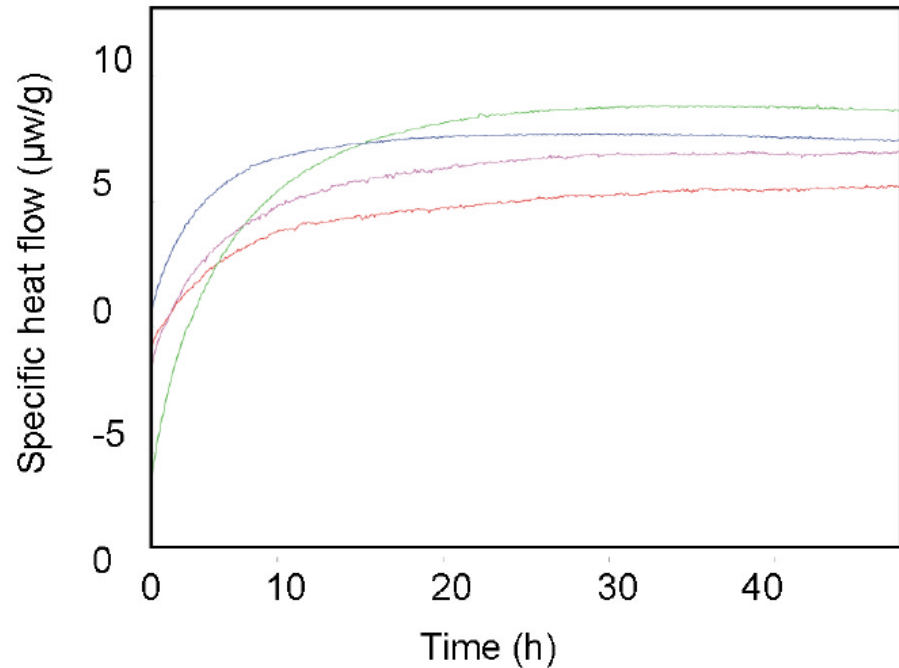


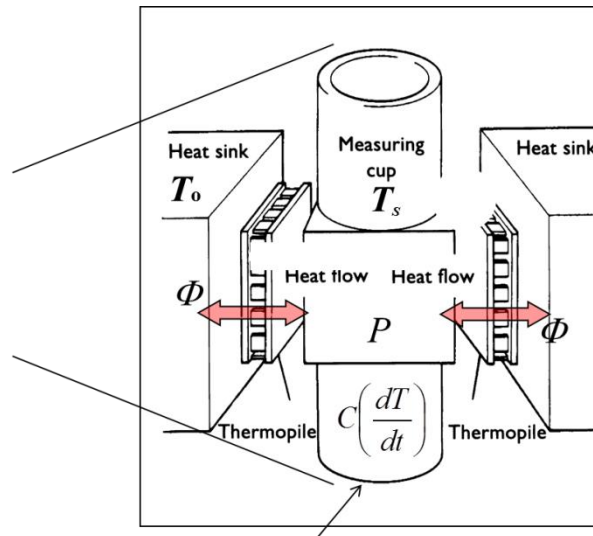
Figure 1. Typical microcalorimetric responses for sodium percarbonate stability tests at 40°C.

Sample	Specific Heat Flow at 16 Hours (µW/g)	Specific Heat Flow at 48 Hours (µW/g)	Pass/Fail
1	4.4	5.6	Pass
2	7.5	8.6	Pass
3	7.3	7.4	Pass
4	6.0	6.9	Pass

Calorimetric / pressure measurements

METHODOLOGY

Principle of twin-heat conduction calorimeters



Calibration heater mounted inside the bottom of the ampoule holder

- The measurement assembly is contained in a highly temperature regulated environment.
- The measured sample is incubated in an ampoule serving as the calorimetric vessel.
- As a sample produces or consumes heat a gradient is formed between the sample and the environment.
- The gradient results in a heat flow between the sample and the environment:

$$\phi = G(T_s - T_0)$$

- After calibration this flow is quantitatively measured in real-time by a battery of thermoelectric devices.
- A heat balance governs the situation in the sample vessel:

$$P = \phi + \tau \frac{d\phi}{dt}$$

- The time constant, τ , is normally in the range 80-200 seconds.

Heat production rate \Leftrightarrow Process rate

$$\frac{d\xi}{dt} = k(T) \cdot f(\xi)$$

$$P(T, \xi) = \frac{d\xi}{dt} \cdot \Delta H$$

ξ = extent of reaction (or alternatively, the amount or concentration of a reactant, intermediate or product)

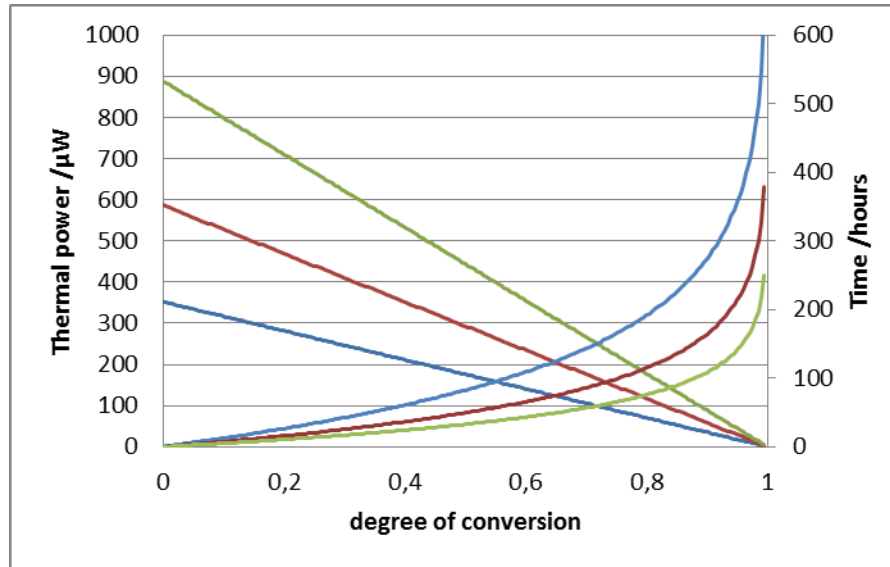
$$P(T, \xi) = \Delta H \cdot k(T) \cdot f(\xi)$$

Enthalpy \rightarrow
Thermodynamic
Information

Reaction rate \rightarrow
Kinetic
Information

Concentration \rightarrow
Analytical
Information

$$\Delta n \propto \Delta \xi = \int_{t_0}^t P(T, \xi) dt / \Delta H$$



Hydrolysis of acetyl salicylic acid

Pseudo 1-order reaction. Illustration of the hydrolysis of aspirin as measured by isothermal microcalorimetry at three different temperatures: 25°C (blue), 30°C (red), and 35°C (green).

TAM IV – Features

- New wider temperature range of 4 to 150 °C extends testing capabilities for applications such as reaction kinetics studies and real-world low temperature storage stability.
- The thermostat design incorporates thermistors for temperature sensing and regulation in the order of 10^{-4} K.
- Plug-and-play calorimeters for easy installation.
- High-speed USB to PC communications.
- New Accessory Interface box with capacity for up to eight modules.
- New voltage I/O Module for interfacing up to three independent probes/sources such as pH-probe or light source.
- TAM Assistant - control and data analysis software.



Calorimeters for TAM IV



Nanocalorimeter
<5 ml sample size

Microcalorimeter
<20 ml sample size

Multicalorimeter
6 calorimeters <5 ml
3 calorimeters < 20 ml

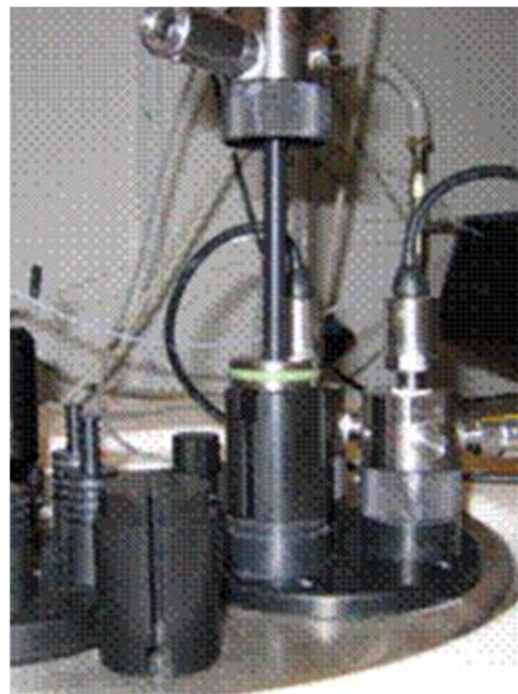
Macrocalorimeter
< 120 ml

Precision Solution
Calorimeter
Precision Titration
Calorimeter

The Sample Handling Systems

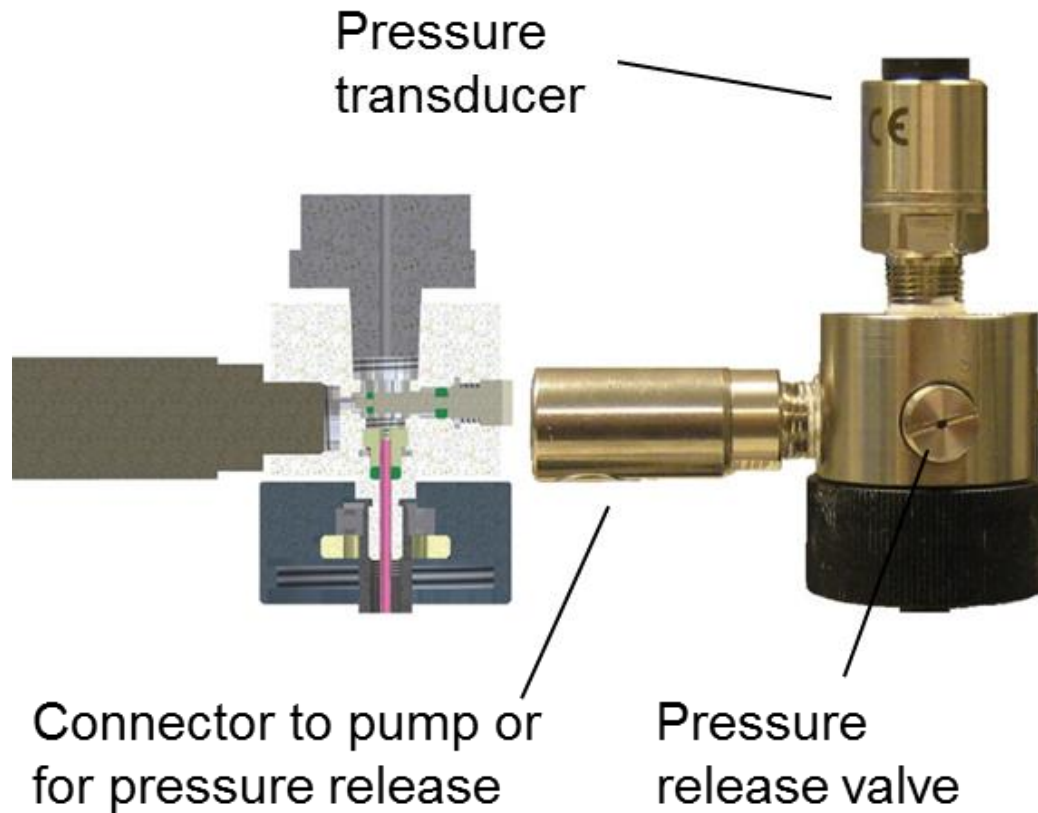
- Closed or sealed (static) Ampoules
- Open ampoules - Micro Reaction System
 - Perfusion
 - RH perfusion
 - Titration
- Micro Solution Ampoule





The pressure ampoule

The 20-ml stainless steel reaction vessel is attached to the top part of the device, where after the assembly is thermally equilibrated before introduced to the calorimeter measuring position. The last point in the sequence is to connect the pressure sensor to its electronic interface.

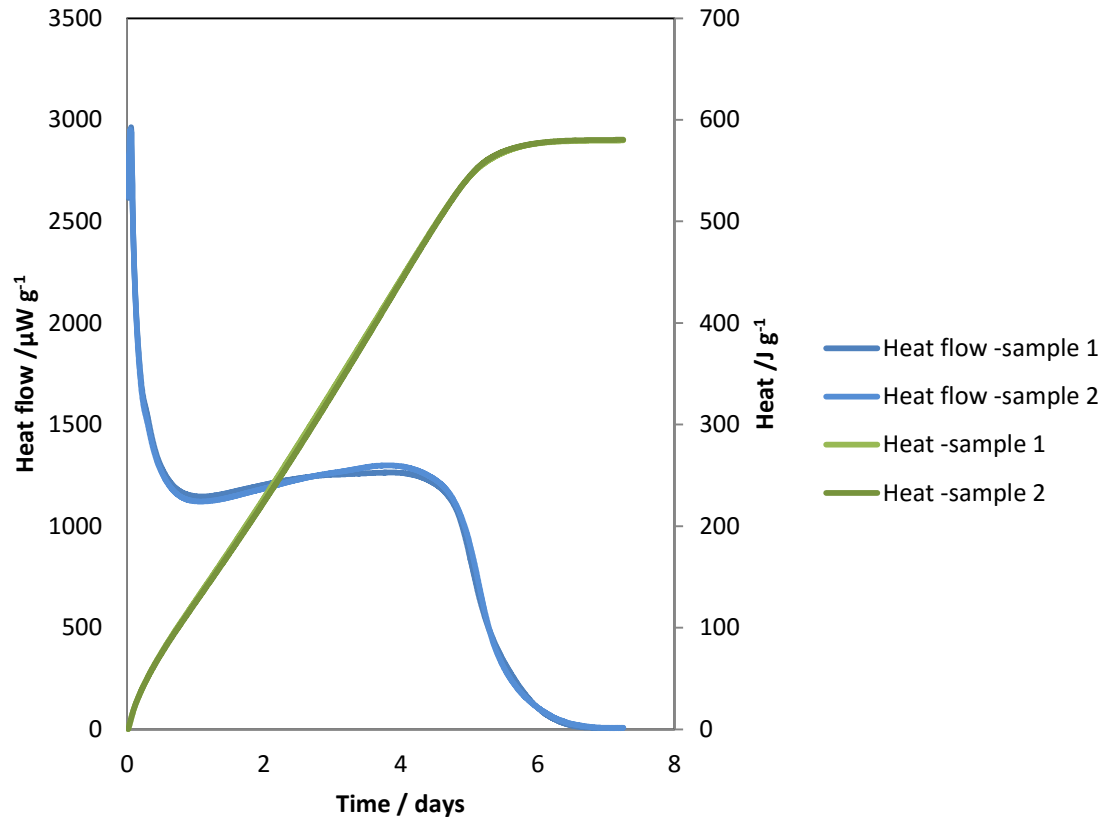


Top part of the pressure ampoule

The top part consists of a spring loaded back valve that release pressure at a certain value (e.g. 10 bars) for safety. The pressure transducer is mounted at the top. An outlet connector on the side may be used for evacuation or pressure release.

Calorimetric / pressure measurements

RESULTS OF SPC MEASUREMENTS



SPC degradation – heat flow and cumulative heat vs time graphs

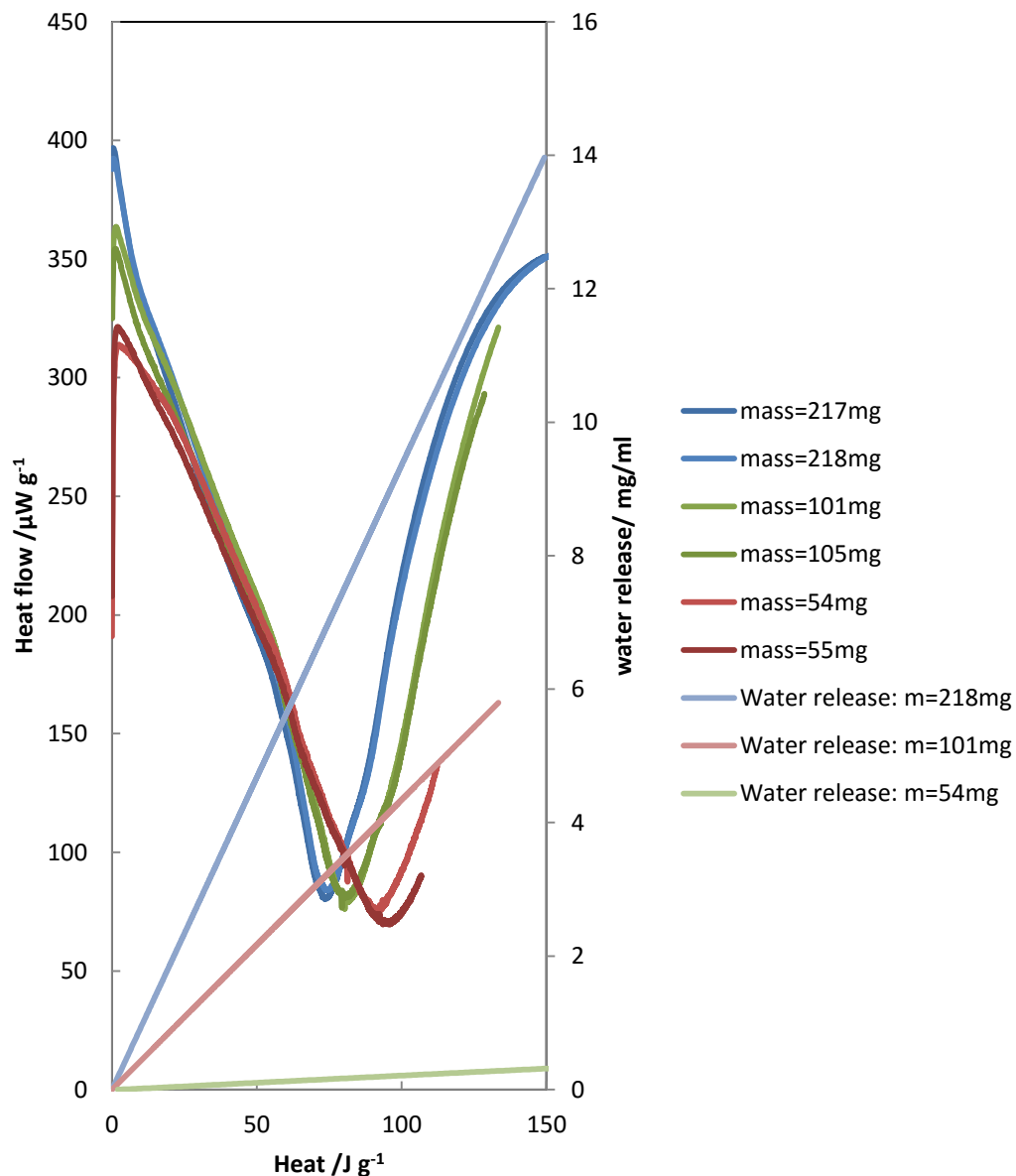
Approximately 200 mg sample in 4-ml glass vials serving as the calorimetric vessels. The measuring temperature in this example was 50 °C.

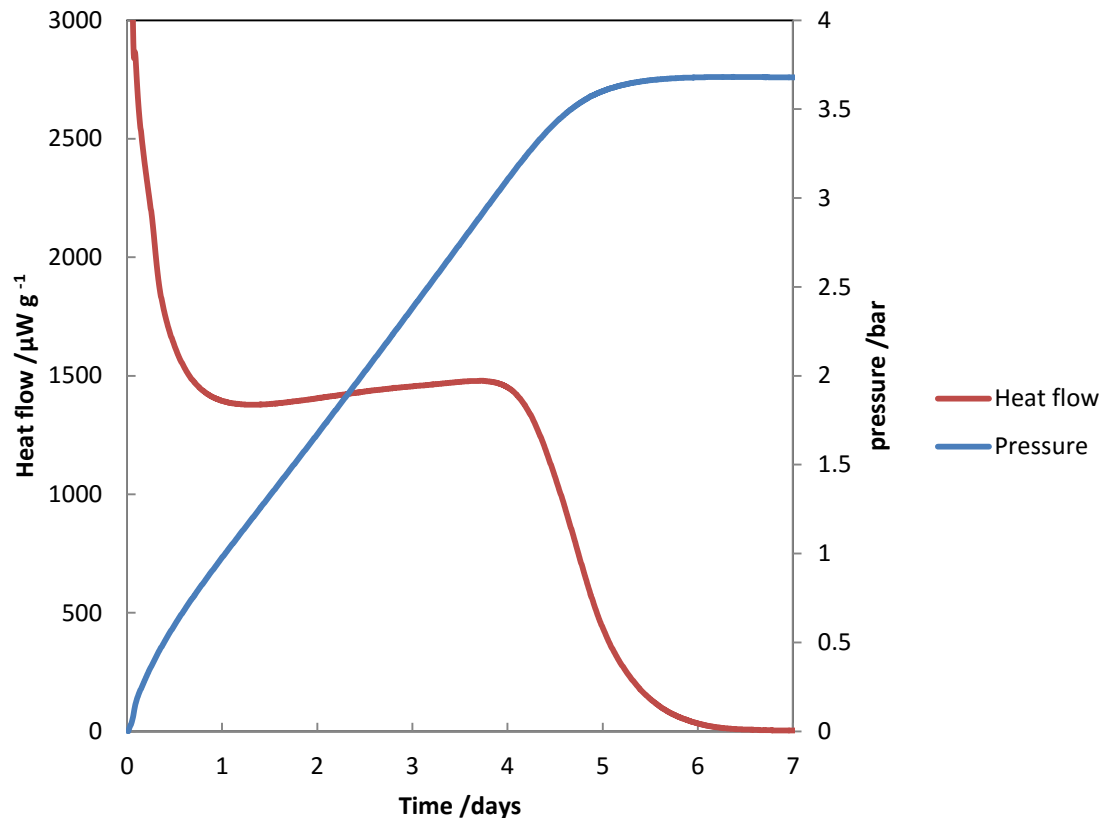
Influence of mass/volume ratio

Heat flow data versus heat at 40°C, below ~25% conversion (corresponding to 150 J g⁻¹).

It can be seen that the acceleration of the reaction rate is delayed as the mass is lowered.

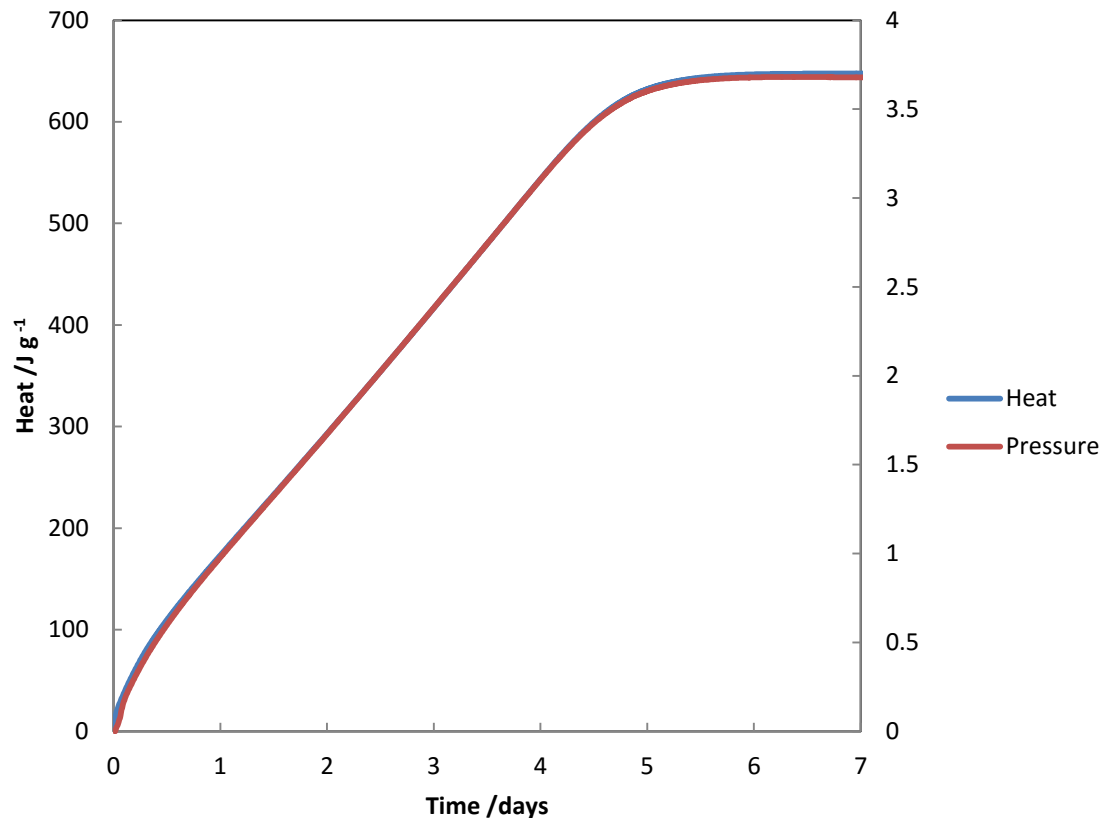
This is most likely due to that the amount of water released in the decomposition process is directly related to the amount of sample per unit of volume at a certain extent of reaction.





Heat flow and pressure evolution vs time

The temperature in this example was 50 °C. The pressure increase was observed to be ca. 3.7 bar. This value corresponds quite well to the theoretical value based on the amount of oxygen evolved at completion of the reaction (3.64 bar with $V=0.032\text{dm}^3$ and $m=0.91\text{g}$).



Pressure and Cumulative Heat

The heat flow integrated vs time giving the cumulative heat. The cumulative heat compared to the evolution of the pressure during the degradation. The two lines nearly overlap showing that both process indicators reflect the extent of the reaction in a similar way.

Heat divided by pressure

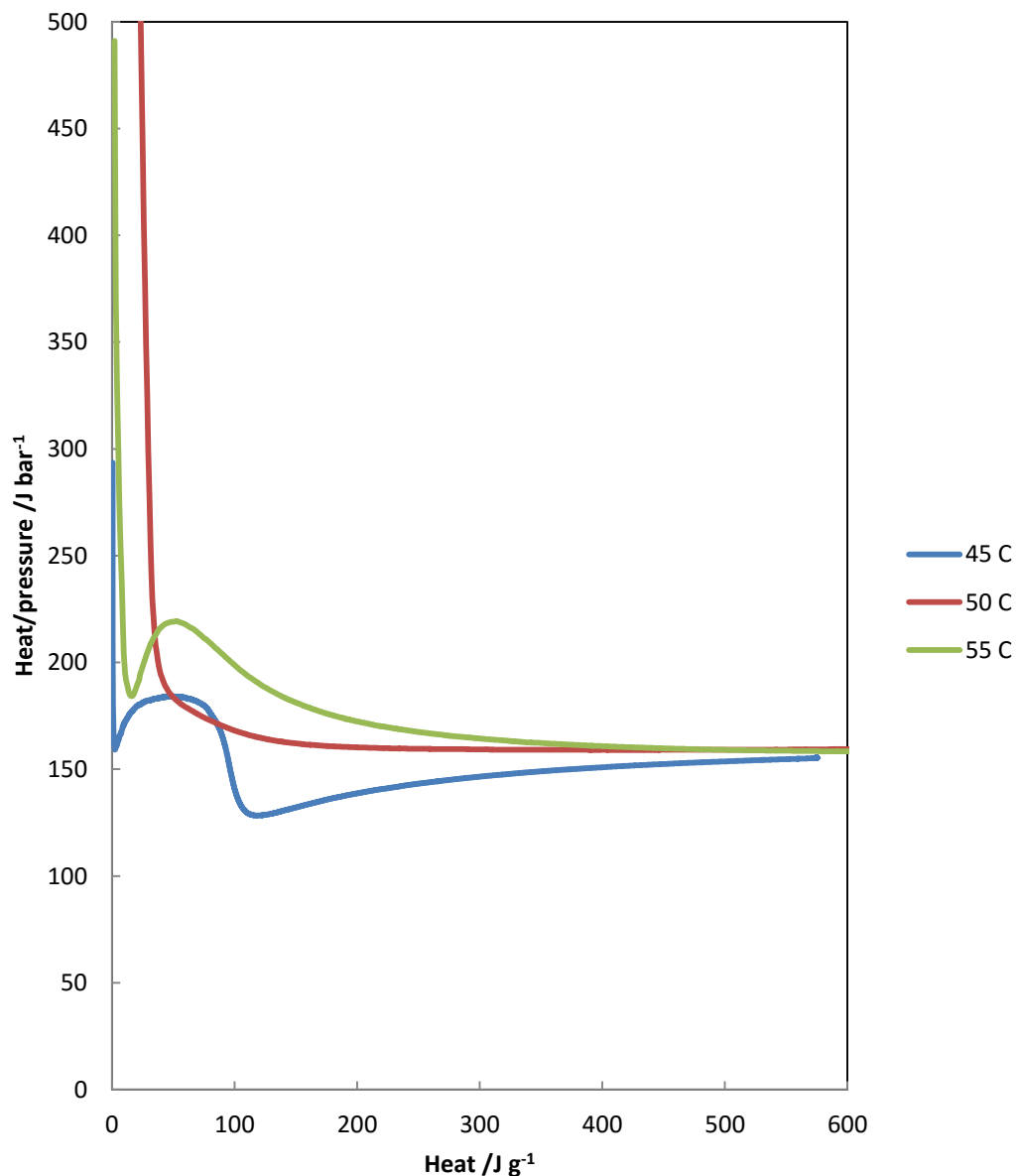
The graph shows the cumulative heat divided by the pressure.

The lines conform towards a common value towards the end of the measurement of $\sim 160 \text{ J bar}^{-1}$.

By attributing the pressure increase to the evolution of oxygen we can estimate an enthalpy change of the process:

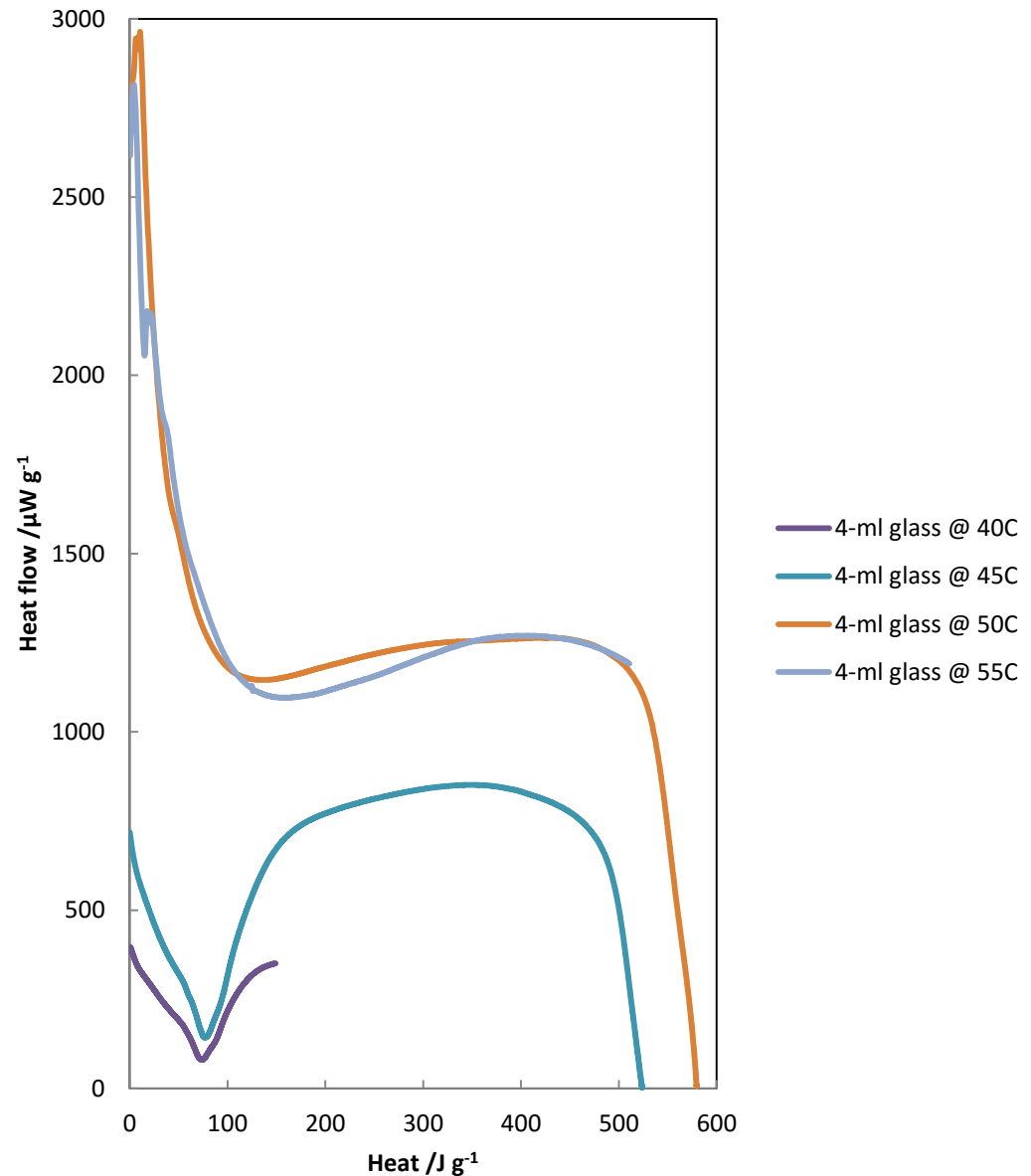
$$\Delta H = \frac{\text{Heat}}{p} \cdot \frac{RT}{V} \cdot \frac{3}{4} = 98 \frac{\text{kJ}}{\text{mol}}$$

The factor $\frac{3}{4}$ is the stoichiometric relationship between O_2 and SPC.



Temperature dependency

- The heat flow vs heat graphs at 4 different temperatures in the range 40-55 °C.
- The reaction characteristics change between 45 and 50 °C.
- It is clear that the reaction rate doesn't obey Arrhenius behaviour.
- A possible reason for the complex reaction is the role of water regarding the partitioning between the bound state in the sample and the head space of the ampoule.



References

- Galwey, A.K. and Hood, W.J. (1979) Thermal decomposition of sodium carbonate perhydrate in the solid state. J. Phys. Chem 83(14).
- Popov, Muravlyansdsky and Phipps. Thermometric Application note 22034.

Thank you

- SPC degradation in a closed system depends in a complex way on water partitioning and the establishment of a product surface layer.
- It has been shown that small variations in sample mass with constant volume has an impact on the kinetics.
- The enthalpy change calculated from calorimetric and pressure data results in 98 kJ mol^{-1} , compared to 94 kJ mol^{-1} for calorimetric data for which the reaction has been monitored to completion.
- The reaction doesn't obey simple Arrhenius behaviour, possibly due to the role of water.
- Microcalorimetry in combination with pressure measurements can provide valuable insight into the understanding of the reaction mechanism.
- Full understanding of the degradation of SPC is still not complete.

