

Measurements of water adsorption kinetics by heat flow evaluation of large pressure jumps to isobaric conditions

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Introduction

Saving energy is one of the most pronounced aims of scientific effort in the last decade observing a growing world population and a decline of fossil primary energy carriers. A remarkable part of energy is used for heating and cooling purposes. Savings can be realized in this field by the technology of sorptive heat storage and sorptive cooling. Here, the physisorption of small molecules, especially water molecules, can be exploited by profiting from the involved energetic contributions such as heat of adsorption, condensation and hydration. For this purpose we fabricate micro-macroporous composites of MOFs and zeolites on cellular supports.

To evaluate the produced composites, it is important to characterize their detailed sorption properties. In addition to equilibrium values such as the energy storage density, sorption kinetics such as the heat release rate are equally important.

Advantages and challenges of LPJ to isobaric conditions

In a conventional large pressure jump (LPJ) experiment water vapor is collected in a large dosing chamber with a known volume. The sample is in an evacuated separated chamber. Then the measurement of adsorption is initiated by the opening of a solenoid valve. The steam flows into the sample chamber and the pressure drops continuously. From the curve progression of the pressure, the recorded amount of adsorbed water is calculated.

However, the sorption kinetics is dependent on the water partial pressure (driving force). Unfortunately, in a conventional LPJ the boundary conditions are not constant, which results in heat and mass transfer "constants", which represent an average value for a certain pressure range. An infinitely large dosing chamber would create constant conditions, but no pressure curve could be recorded during the experiment. Another possibility for a constant ambient pressure is the control via a PID-controlled needle valve between the sample chamber and the evaporator. A possible implementation is shown in the flow diagram (Fig. 1).

Following our concept, the determination of the adsorbed amount of water is not possible from calculations of the ideal gas law. This implements that a direct detection of the adsorbed amount would be necessary. The use of mass flow controllers for this purpose is questionable. Here an unfavorable response time at the beginning of an LPJ results in large errors concerning the recording of water mass. Therefore we use heat flux sensors to determine the sorption kinetics.

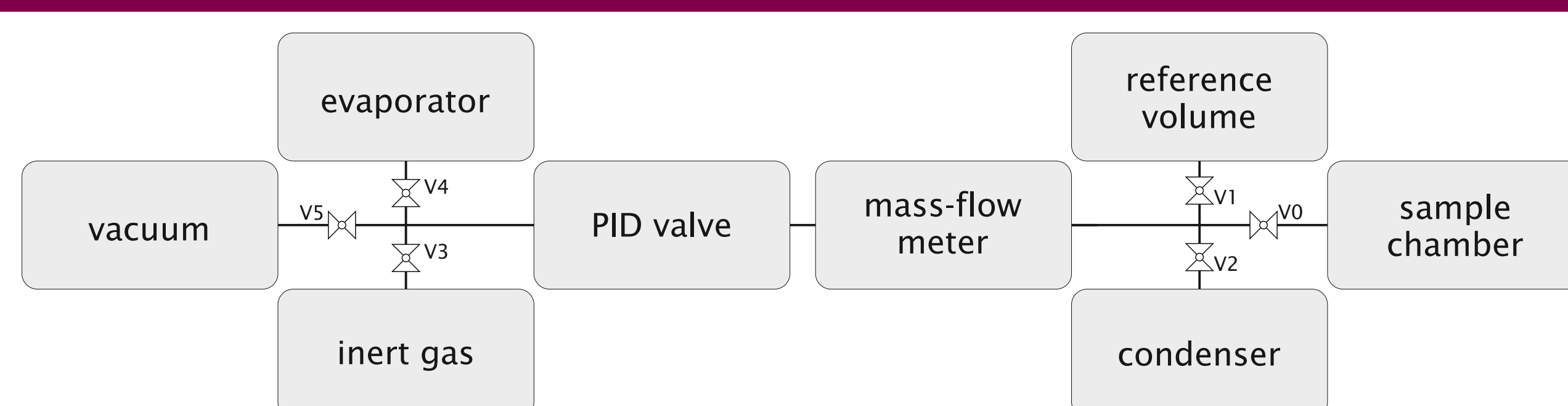


Fig. 1: Flow chart of sorption test device "STS2".

Custom made instrument "STS2"

The sample environment and the schematic structure of the sorption test device "STS2" is shown in Fig. 2. Not shown are the evaporator, the condenser, the temperature control of the sample stage with an external thermostat, the data acquisition system, the heated housing and the insulation of the device.

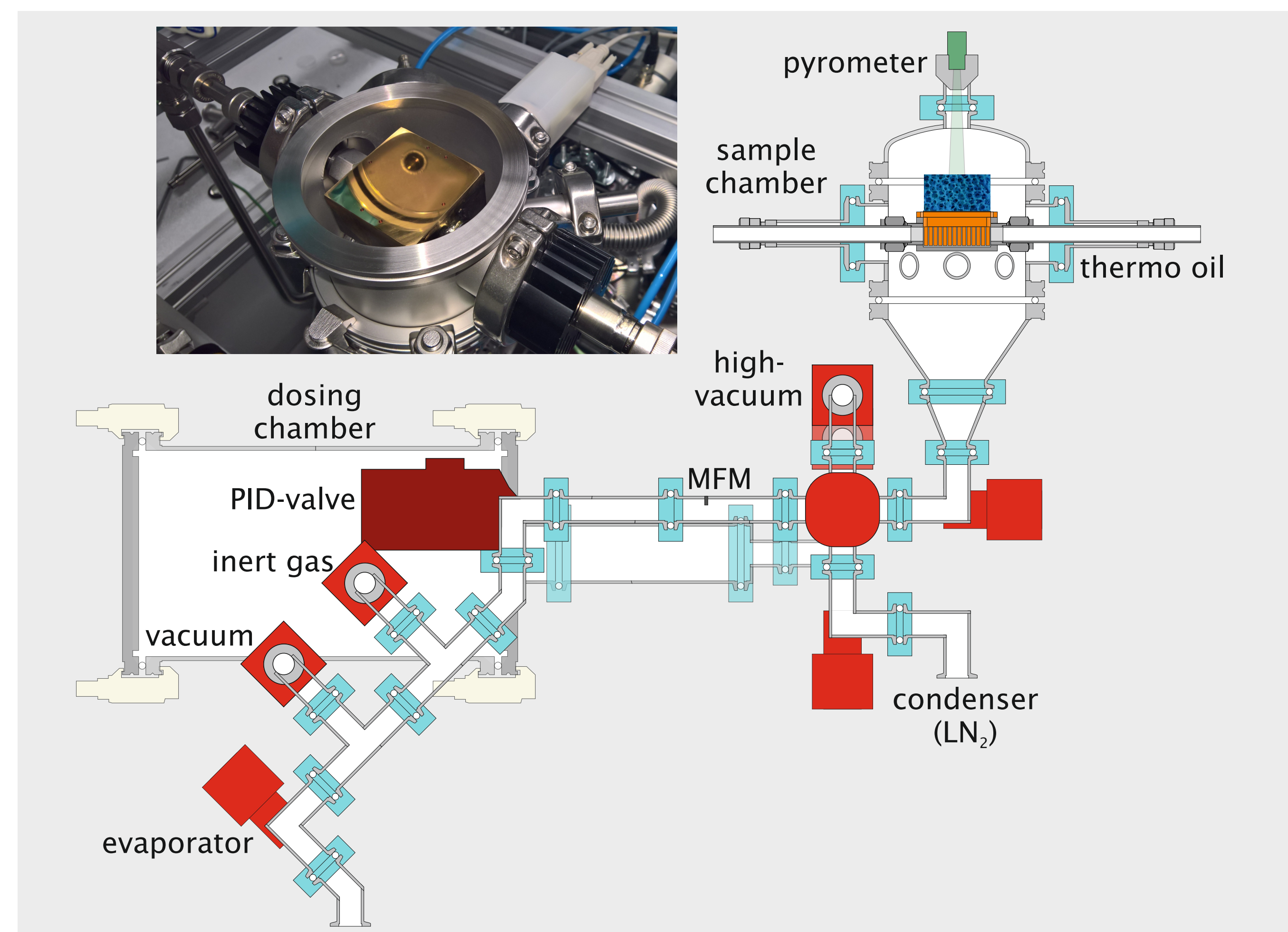
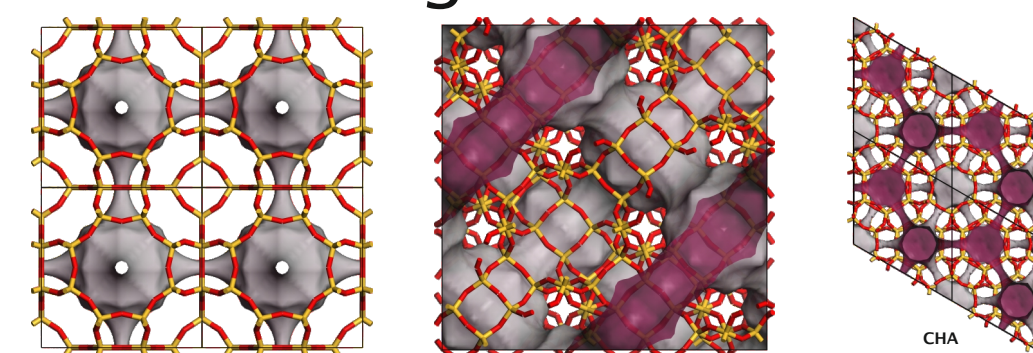


Fig. 2: Schematic structure of sorption test device "STS2". Photo of the sample stage (inset).

Three-dimensional samples

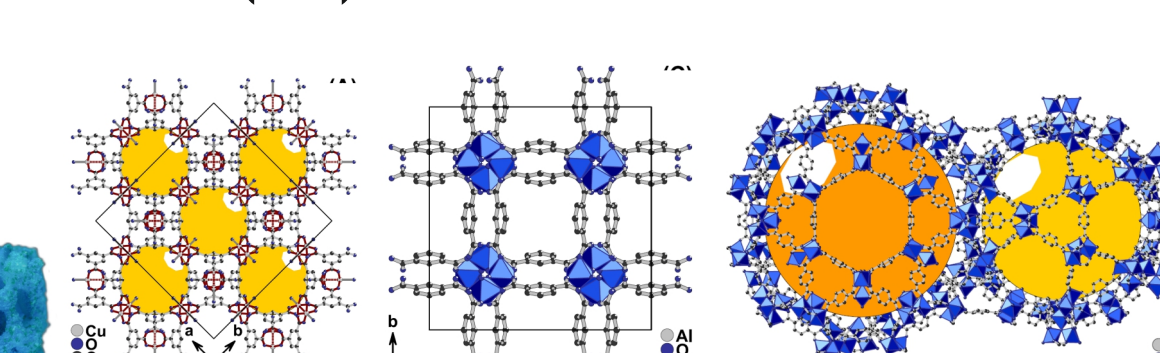
zeolites

Porous aluminosilicates and aluminophosphates are currently used in heat storage systems. Zeolite A (LTA) and X (FAU), and the SAPO-34 (CHA) are mainly used. Our work focuses primarily on dealumination (modification of the crystal lattice) and the ion exchange.



metall-organic frameworks

MOFs are composed of organic linkers and metal nodes. This "modular principle" leads to structures that can have a large pore volume and a large water absorption capacity. We focus on structures like CAU-10-H, HKUST-1, MIL-100(Fe), MIL-101(Cr) or Al-fumarate.



heatconducting support

composite for heat transformation

To improve the thermal conductivity of an adsorber, macroporous, open foam structures are used. Commercially available foams (metal) and self-made foams (ceramic) are applied.^[1]

As coating methods the direct crystallization (optimal heat transfer between active layer and carrier) or binder-supported methods (broad applicability) are used.

Improvements compared to "STS1"

- new sample chamber with smaller volume
- new sample stage with high mass of copper (coated with gold)
- higher surface for heat exchange (oil to copper)
- 1/2 inch pipes for thermal oil
- temperature measurement contactless (infrared pyrometer)
- additional temperature points with pt100
- additional condenser (desorption measurements with MOFs)

Requirements for the sample

- maximal size: 50 x 50 x 50 mm
- minimal size: diameter 15 mm (for temperature measurement with IR)
- non-metallic surface (for temperature measurement with IR)
- water uptake: 0.1 - 20 g per sample
- maximal water uptake rate: 20 g/min
- desorption temperature below 180 °C
- no outgassing at desorption temperature (high vacuum compatible)

References

[1] Ulf Betke, Michael Klaus, Jakob G. Eggebrecht, Michael Scheffler, Alexandra Lieb, „MOFs meet macropores: Dynamic direct crystallization of the microporous aluminum isophthalate CAU-10 on reticulated open-cellular alumina foams“, *Microporous and Mesoporous Materials*, 2018, 265, 43.