Kinetic Analysis of Sensor-Gas-Calorimeters as Linear Passive Systems

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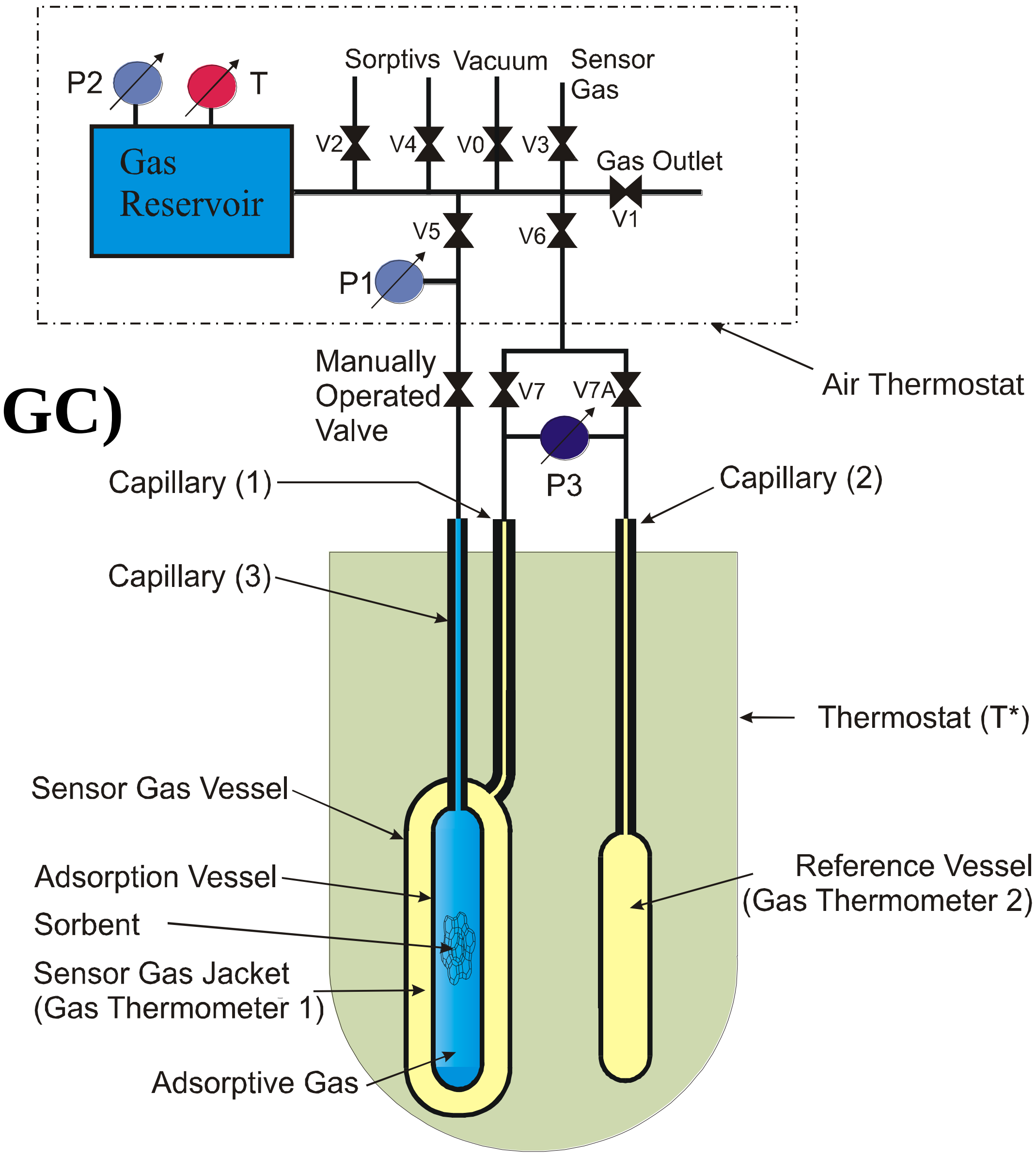
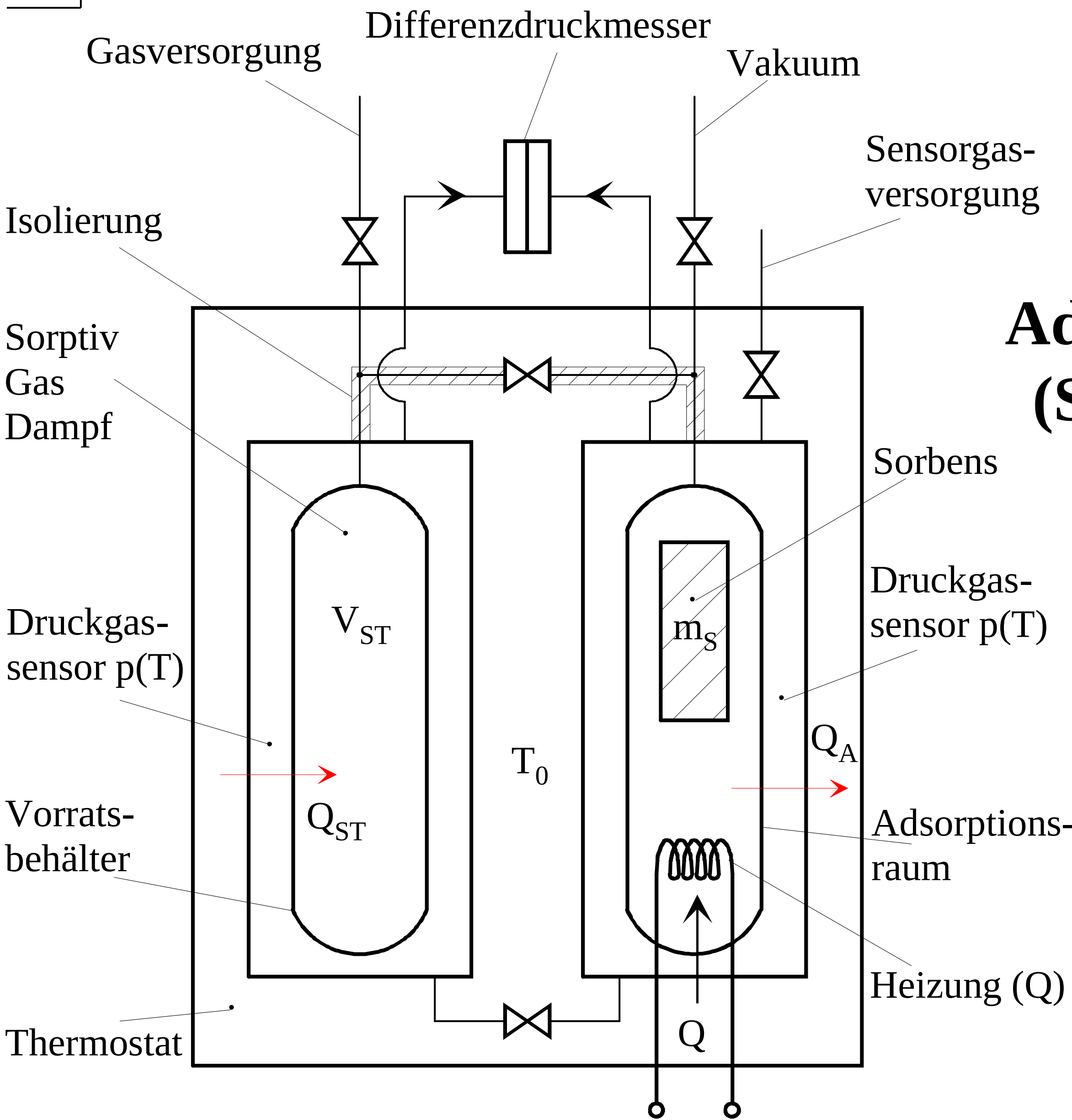
1. Sensor-Gas-Calorimeters (SGC)
2. Calibration experiments
3. Thermodynamics of heat transfer processes
4. Theory of Linear Passive Systems (LPS)
5. Simple models and their inversion
6. Conclusions

Schematic diagram of a Sensor Gas Calorimeter (SGC)





Sensor-Gas-Adsorptionskalorimeter (SGAK) © IFT 2003

$$H^f - H^a = Q_A - Q_{ST}$$

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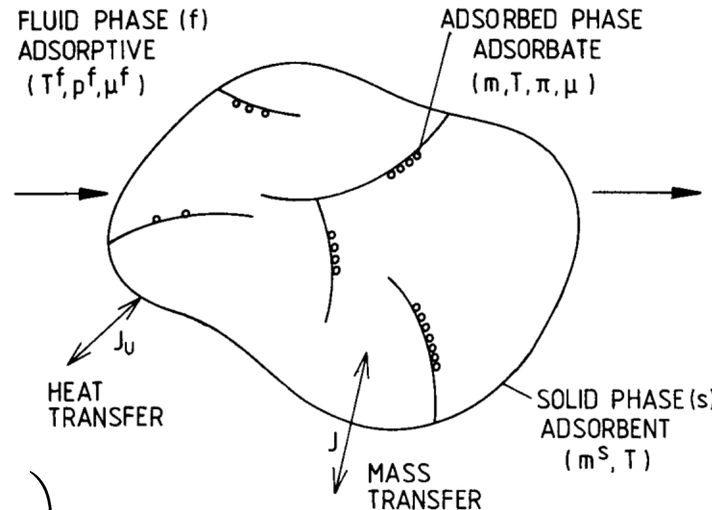
Non-Isothermal Gas Adsorption Processes



1st Law:

$$\overset{\bullet}{\left(m^s + m^a\right)} = J$$

$$\dot{U}^{sa} = \overset{\bullet}{\left(U^s - U^a\right)} = J_u + h^f J$$

2nd Law:

$$\int_{-\infty}^{\infty} \left(\left(\frac{1}{T} - \frac{1}{T^f} \right) J_u + \left[\left(\frac{\mu^f}{T^f} - \frac{\mu}{T} \right) + h^f \left(\frac{1}{T} - \frac{1}{T^f} \right) \right] J \right) dt \geq 0$$

Process Equations

$$\dot{m} = \beta A \left[-c_p^f \ln\left(\frac{T^f}{T} \right) + R \ln\left(\frac{p^f}{p} \right) + h \left(\frac{1}{T} - \frac{1}{T^f} \right) \right] \qquad \dot{U}^{sa} = \left(h^f - h^a \right) \dot{m} + \alpha A_q \left(\frac{1}{T} - \frac{1}{T^f} \right)$$

Literature: J.U. Keller, Ber. Bunsenges. Phys. Chem. 91 (1987), p. 528.

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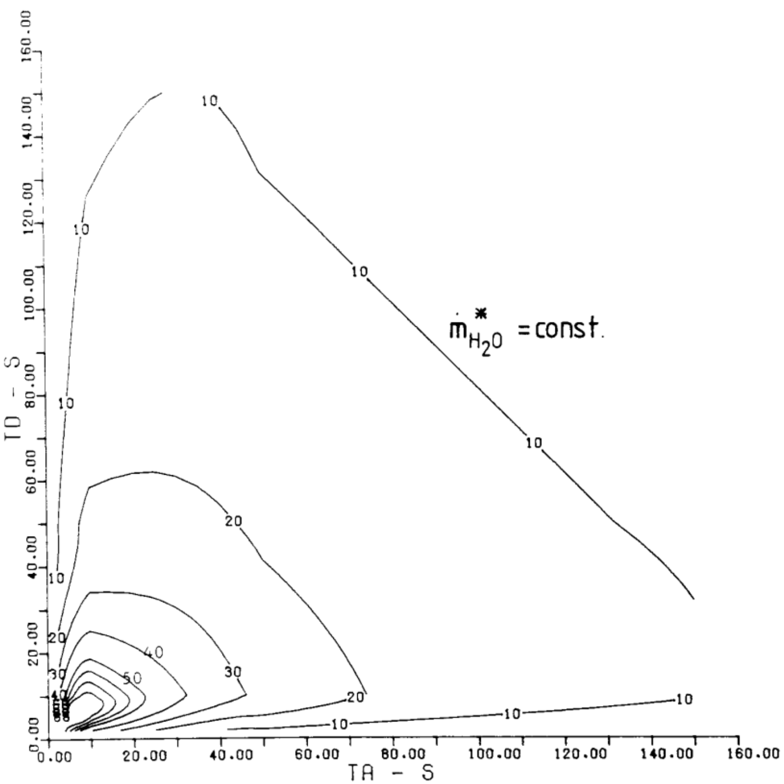
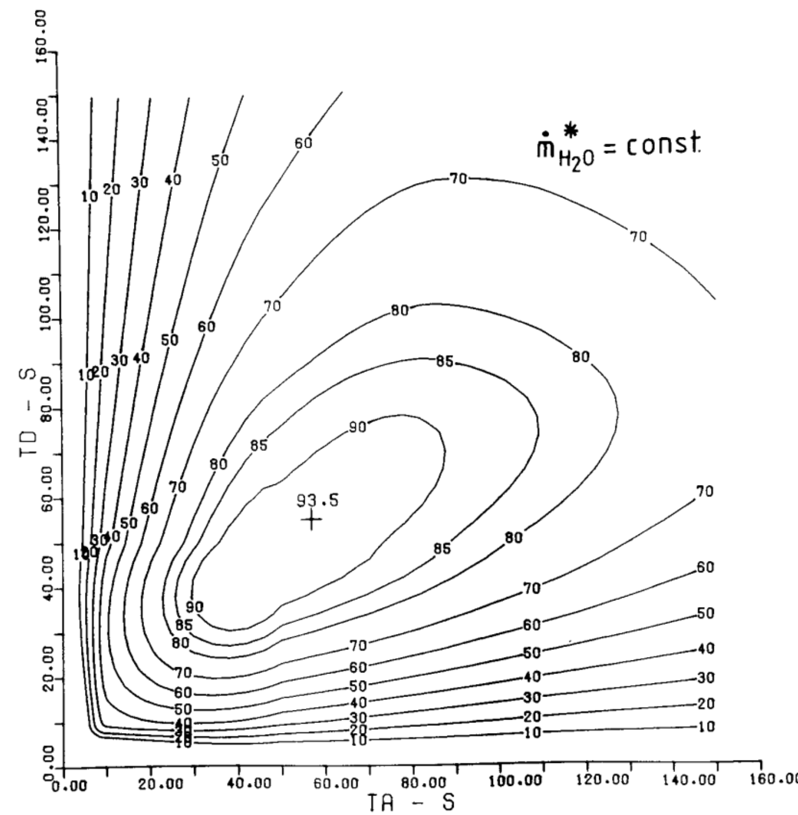
Pressure Swing Adsorption Process (Water Vapor / Aerosorb LR4)

Isothermal Process



Dependence of the asymptotic mass flow $\dot{m}^*_{H20} = (m_{Ad}(t_A) - m_{De}(t_D))/(t_A + t_D)$ on the periods of adsorption (t_A) and desorption (t_D) for the isothermal process in units 10^{-1} g/s kg adsorbens. A maximum value seems to be approached for $t_A = t_D \to 0$.

Non-Isothermal Process



Dependence of the asymptotic mass flow $\dot{m}^*_{H20} = (m_{Ad}(t_A) - m_{De}(t_D))/(t_A + t_D)$ on the periods of adsorption (t_A) and desorption (t_D) for the non-isothermal process in units 10^{-2} g/s kg adsorbens. The maximum value $\dot{m}^*_{max} = 0.93$ g/s kg is realized for $t_A = 57$ s, $t_D = 53$ s.

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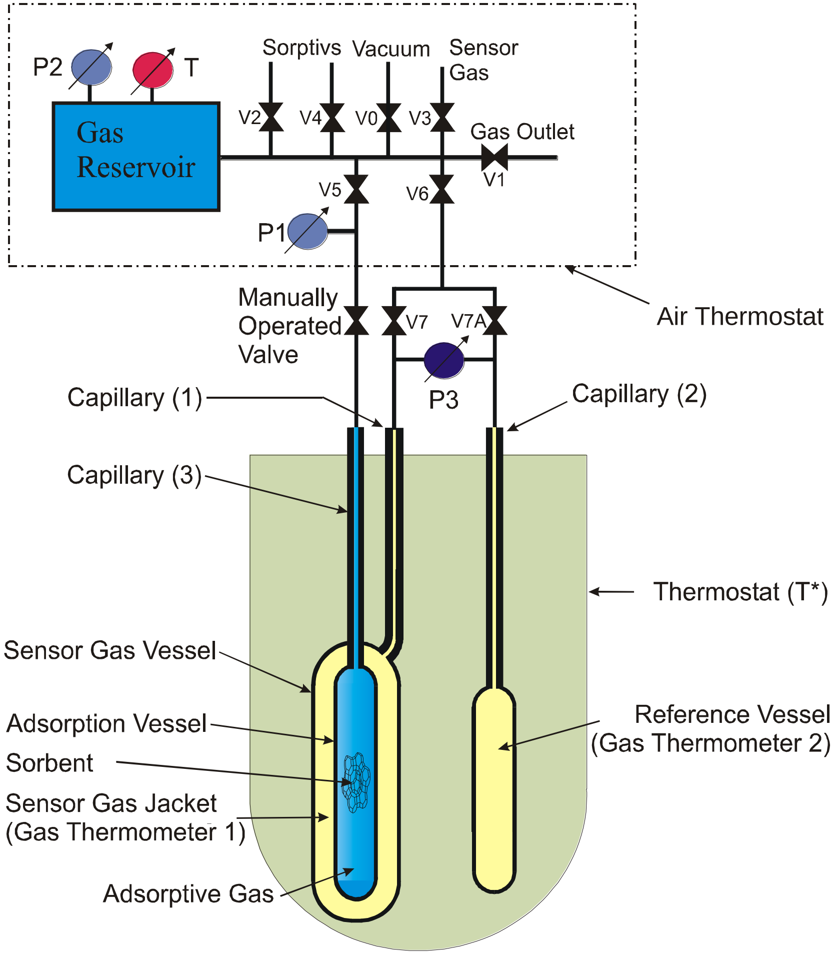
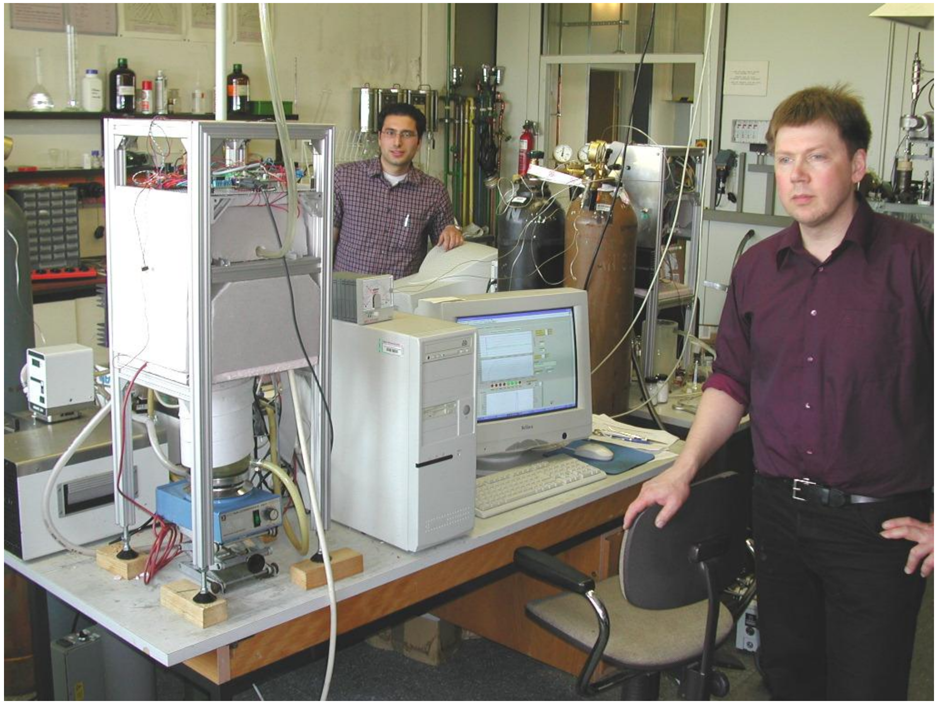
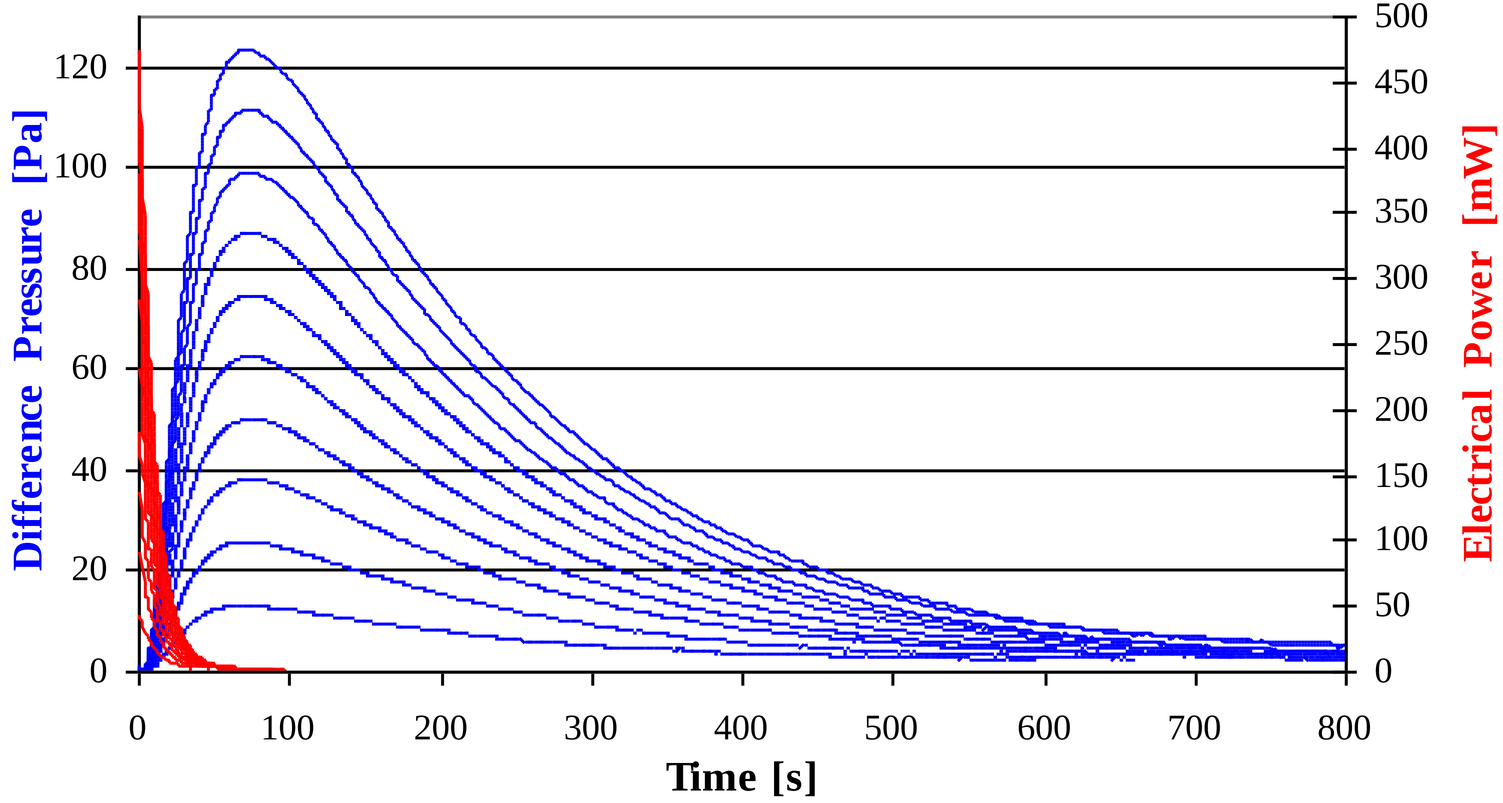


Schematic diagram of a sensor gas calorimeter (SGC)



Sensor gas calorimeter (SGC) for simultaneous measurements of adsorption isotherms and enthalpies.



Calibration experiments in the SGC 0.5J to 5J

Sensor gas N_2 (1.6bar), T=298K, τ=10s

Ohm's heat release (red lines) → Pressure signal (blue lines)

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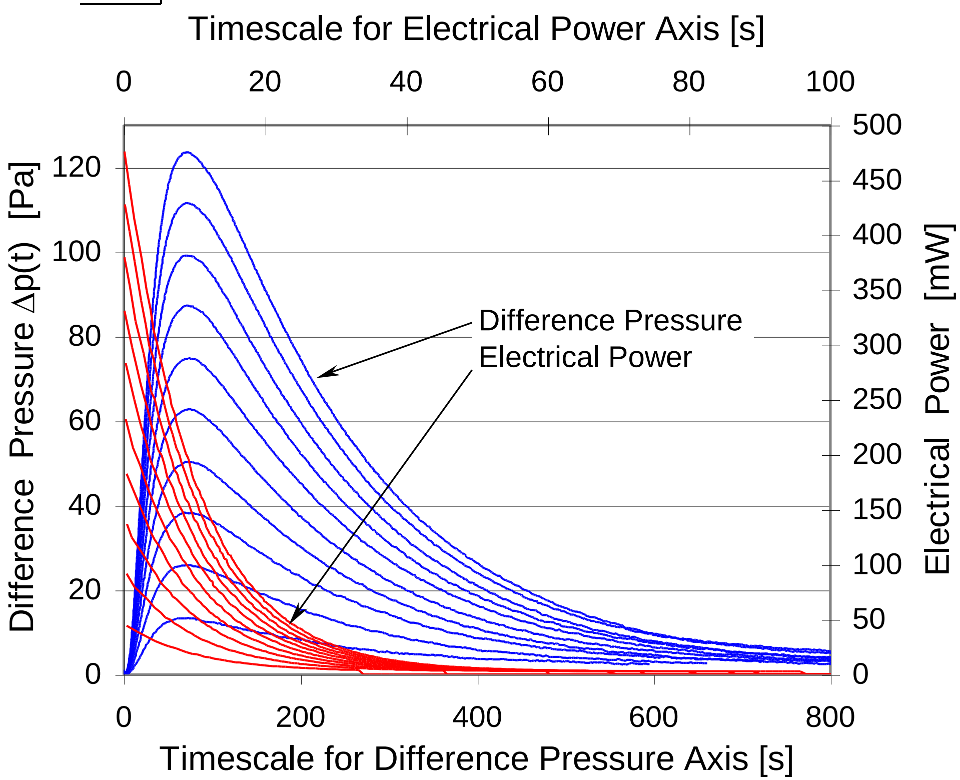
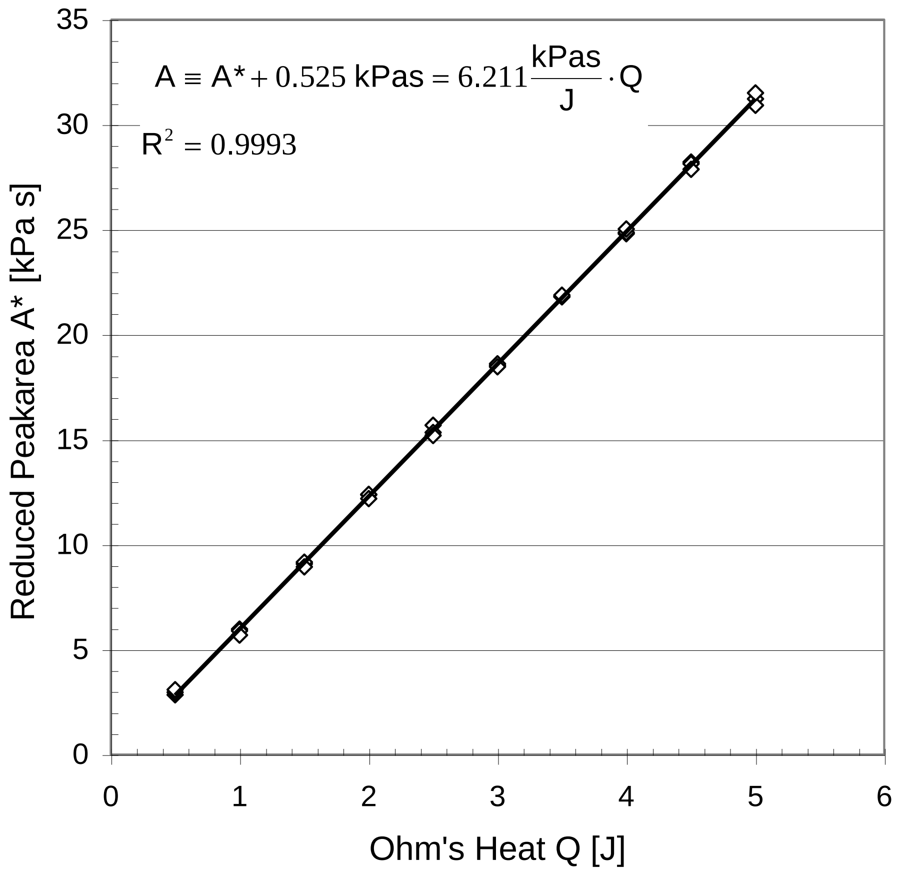
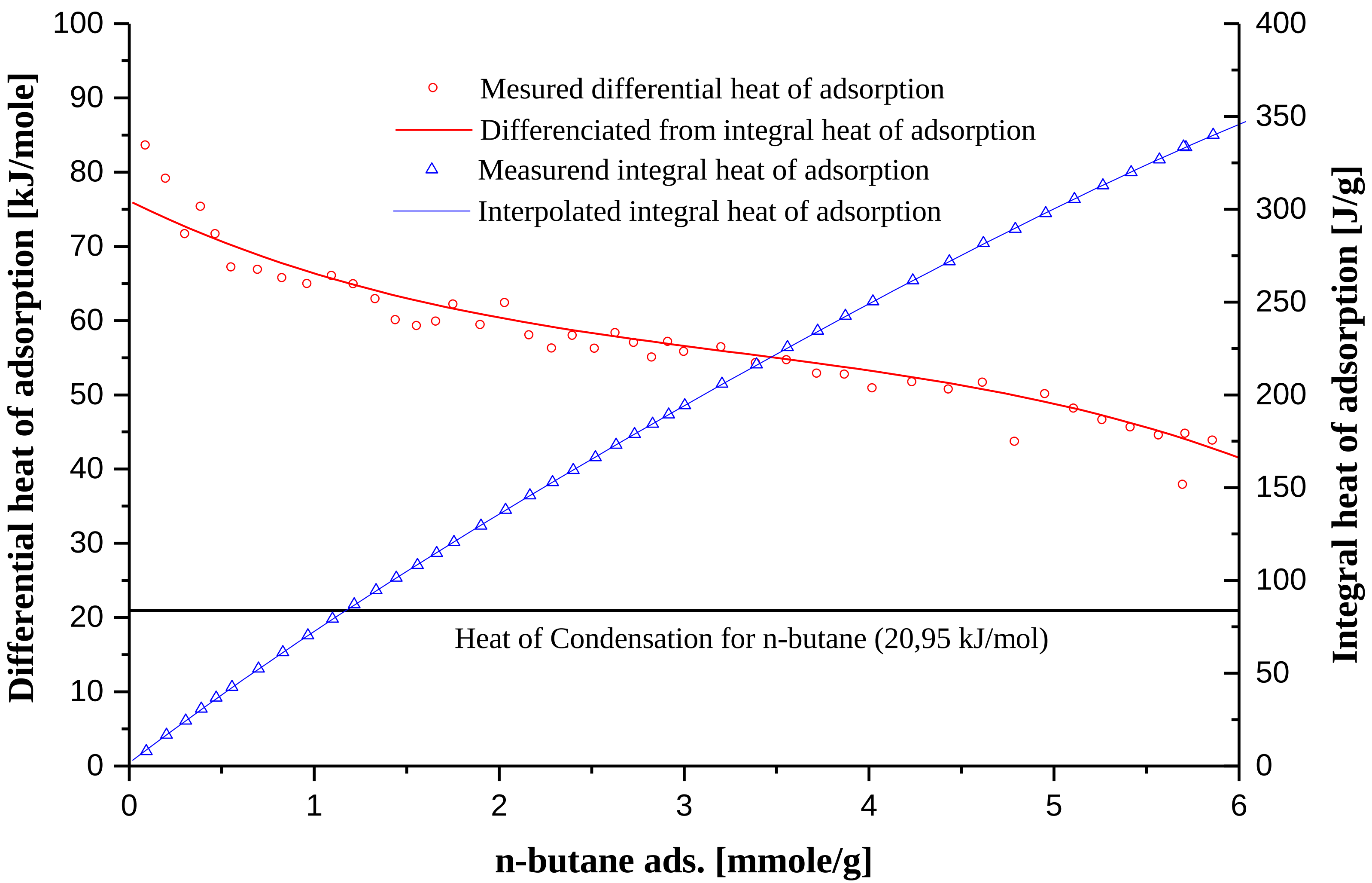


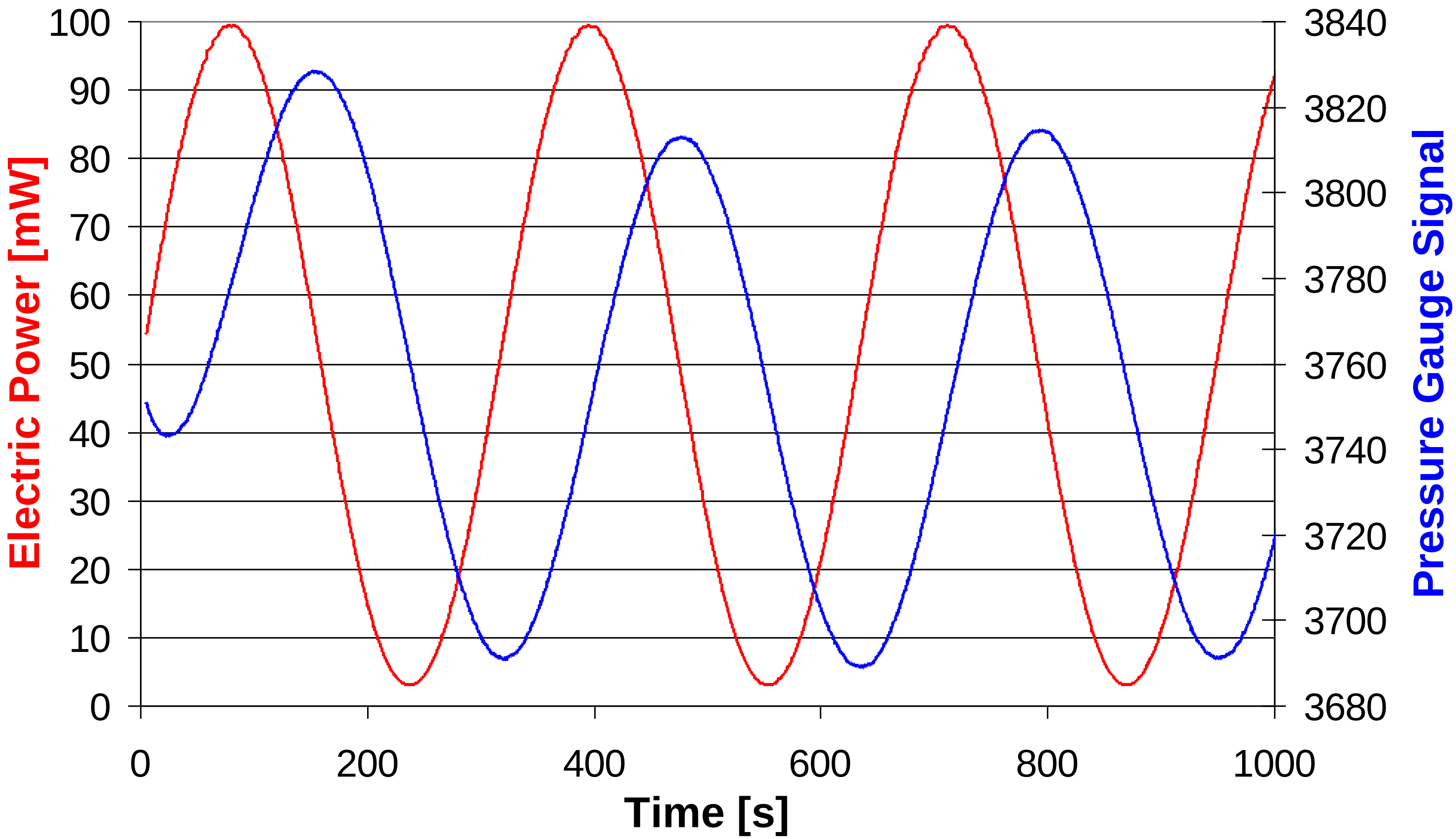
Calibration experiments of the SGC.
Ohm's heat : Q= (0.5, 1.0 ... 5.0)J
Sensor gas: N_2, p*=0.15MPa, T*=298K

Correlation
Peak Area (A / Pas)
Qhm's heat (Q / J)

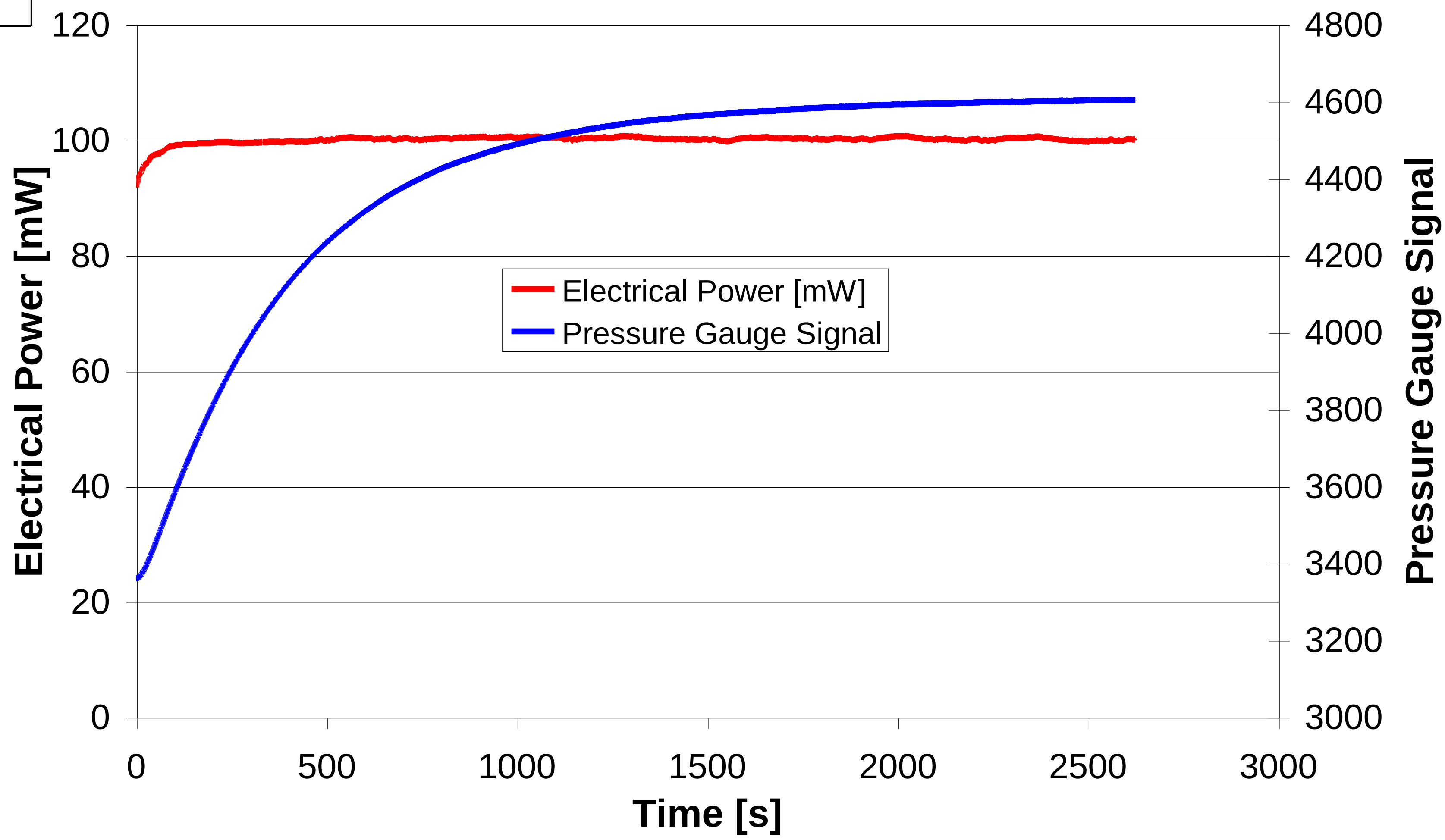




Differential and integral heat of adsorption for activated carbon AC BAX 1500 / n-butane (C_4H_{10}) at 298K.



Calibration Experiment in SGC: Periodic Electric Power / Ohm's Heat and Resulting Pressure Difference



Calibration Experiment in SGC: Step Funktion Electric Power Supply / Ohmian Heat and Resulting Pressure Difference

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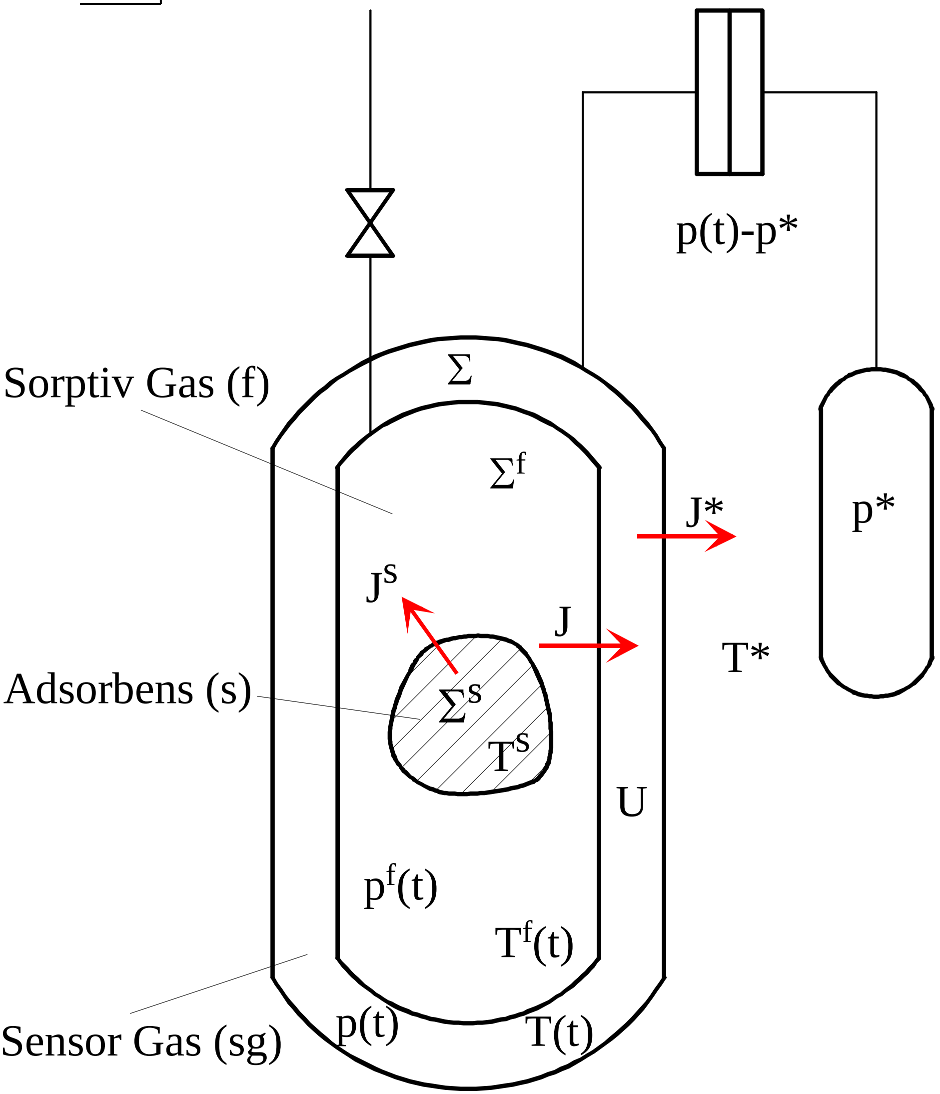

1st Law   CEOS   Heat Transfer

<u>Sorbens / Sorbate</u>

$$\dot U^s = P - J^s = C^s \dot T^s \qquad J^s = L_{sf}(T^s - T^f)$$

<u>Sorptive Gas</u>

$$\dot U^f = J^s - J = C^f \dot T^f \qquad J = L_{fsg}(T^f - T)$$

<u>Sensor Gas</u>

$$\dot U = J - J^* = C \dot T \qquad J^* = L_{sgb}(T - T^*)$$

Heat supply : $P = U_e I_e = (h^f - h^a)\, \dot m^a$

Heat Transfer in the Sensor Gas Calorimeter

Determination of Heat Supply (P) from Sensor Gas Temperature (T)

1st Approximation: $T^s = T^f = T \neq T^*$

$$P(t) = C^{sf}\,\dot{T} + L_{sgb}(T - T^*)$$

2nd Approximation: $T^s = T^f \neq T \neq T^*$

$$P(t) = \frac{C^{sf} C^{sg}}{L_{ssg}}\,\ddot{T} + \left[\left(1 + \frac{L_{sgb}}{L_{ssg}}\right) C^{sf} + C^{sg}\right]\dot{T}$$

$$+ L_{sgb}(T - T^*)$$

Experiment: $T(t), C^{sf}, C^{sg}, L_{ssg}, L_{sgb} \quad : \quad \omega_1, \omega_2$

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Determination of Heat Supply (P(t)) from Sensor Gas Temperature (T(t))

3rd Approximation: $T^s \neq T^f \neq T \neq T^*$

$$P(t) = \frac{C^s C^f C^{sg}}{L_{sf} L_{fsg}} \dddot{T} + \left[\frac{C^f C^s}{L_{sf}} \left(1 + \frac{L_{sgb}}{L_{fsg}} \right) + \frac{C^{sg} C^s}{L_{fsg}} \left(1 + \frac{L_{fsg}}{L_{sf}} \right) + \frac{C^f C^{sg}}{L_{fsg}} \right] \ddot{T}$$
$$+ \left\{ C^s \left[1 + \frac{L_{sgb}}{L_{fsg}} + \frac{L_{sgb}}{L_{fs}} \right] + C^f \left(1 + \frac{L_{sgb}}{L_{fsg}} \right) + C^{sg} \right\} \dot{T}$$
$$+ L_{sgb} (T - T^*)$$

Experiment: $T(t), C^s, C^f, C^{sg}, L_{sf}, L_{fsg}, L_{sgb}$: $\omega_1, \omega_2, \omega_3$

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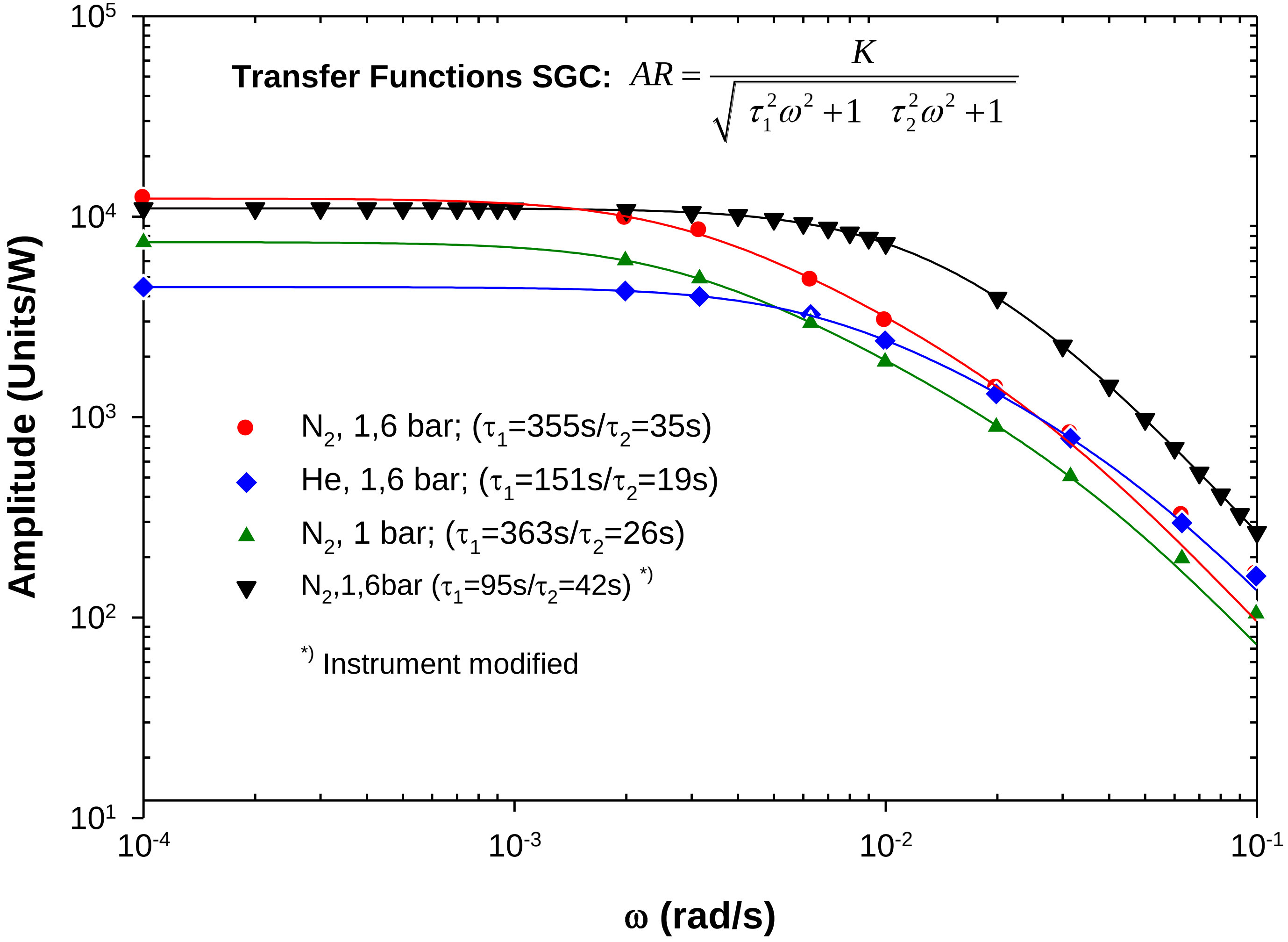
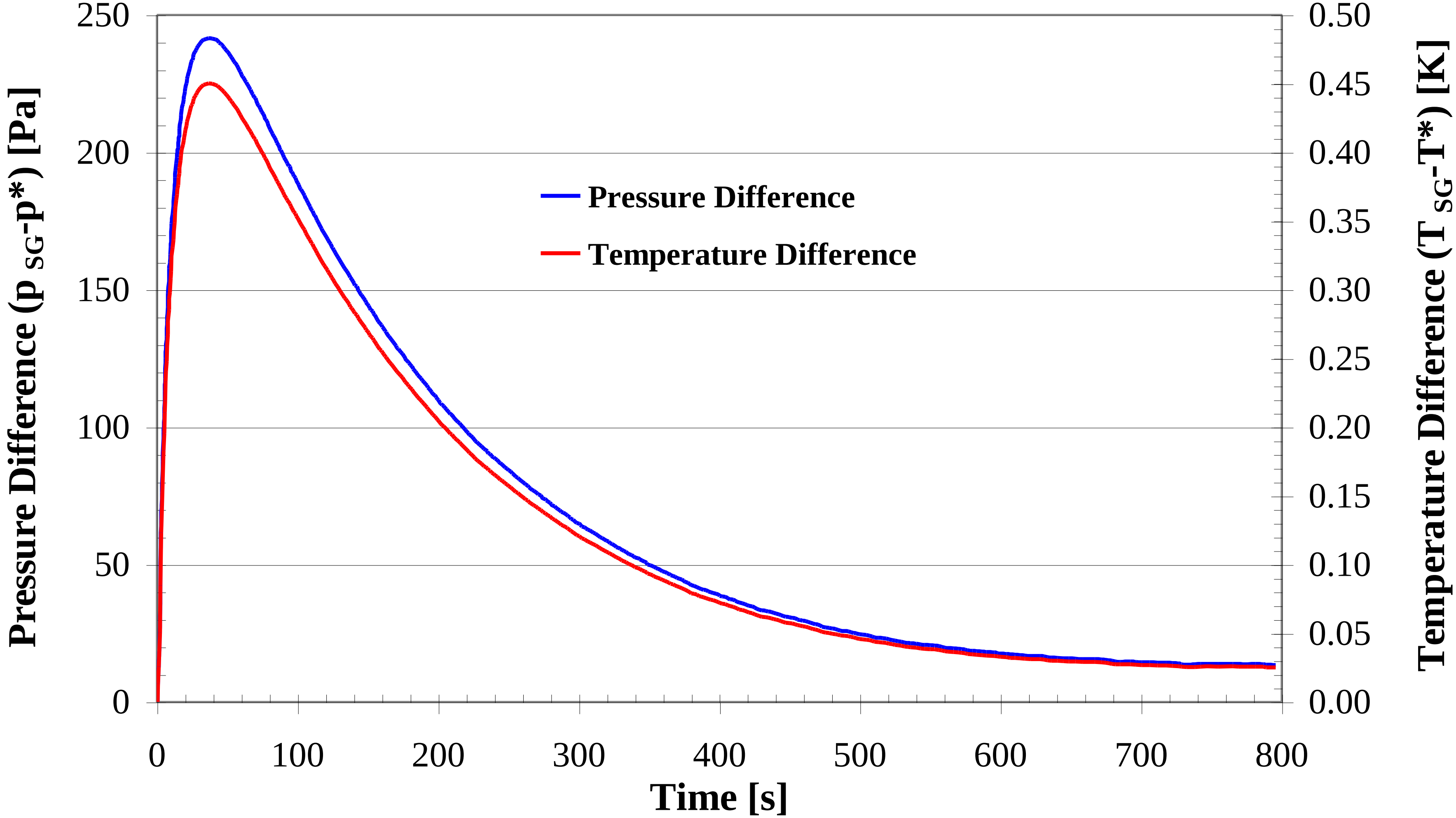


Bode Diagram of SGC (T*=25°C)

Amplitude Ratio $AR \cong (p_{max} - p_{min}) / (P_{e\,max} - P_{e\,min})$



Adsorption of n-butane on AC BAX 1500 at 25°C.
Sensor gas temperature (SGT) and pressure (SGP), $p_{SG}(0)$=1.6bar, N_2.

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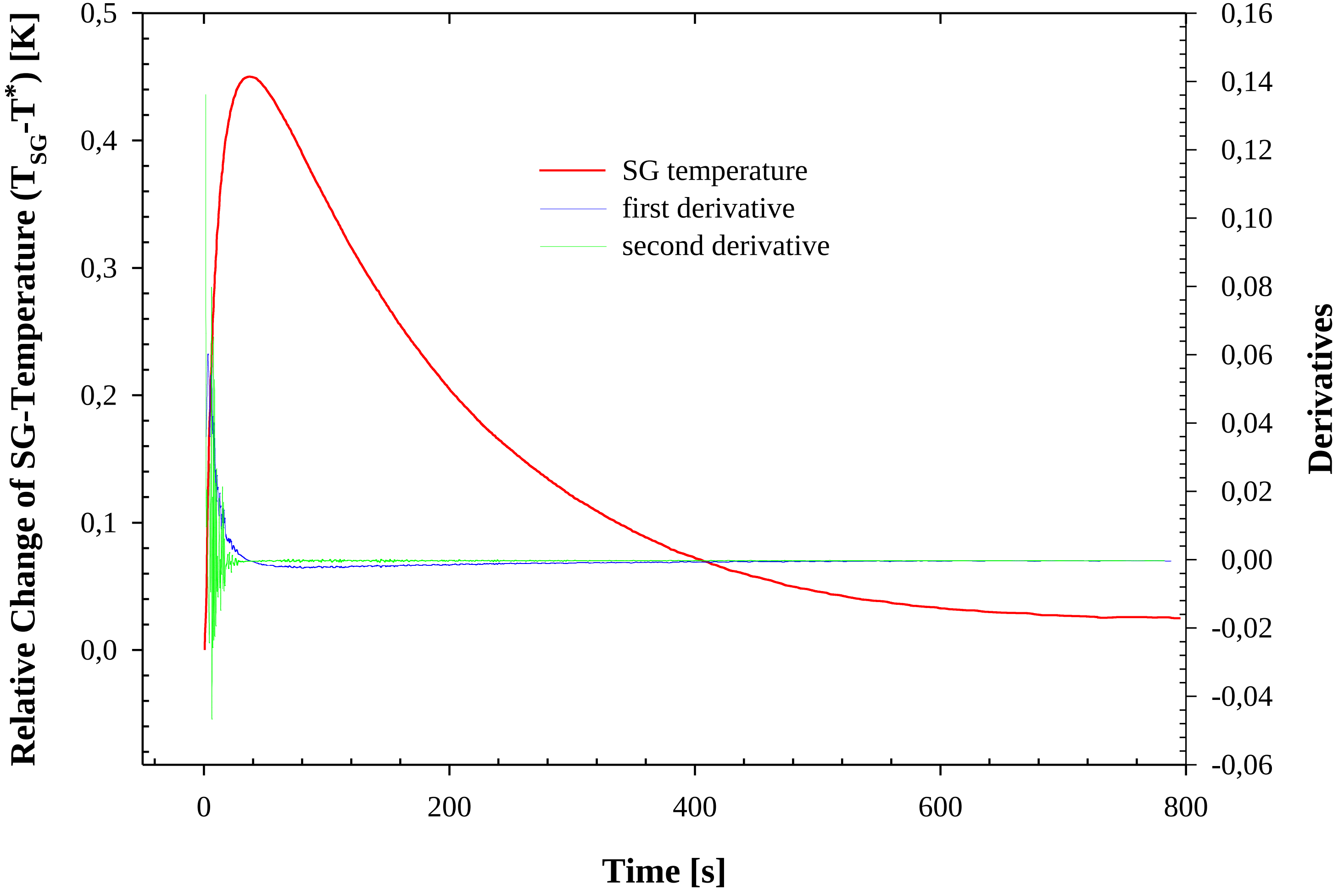

Adsorption of n-butane on AC BAX 1500 at 25°C.
Sensor gas temperature (SGT), p_{SG}=1.6bar, N_2.

Conclusions (SGC – LPS)

1. Non-isothermal gas adsorption process experiments:
   $(p(t) - p^*) \rightarrow (T(t) - T^*) \rightarrow \quad P(t) = (h^f - h^a)\, \dot{m}^a(t)$

2. Calibration experiments Ohm's resistors:
   2^{nd} order model (Bode diagram, $10^{-2}\ s^{-1} < \omega_1, \omega_2 < 10^{-1}\ s^{-1}$)

3. Resonance frequencies (ω_1, ω_2) depend on
   - sorbent (type, m^s)
   - sorptive gas (type, T, p)
   - sensor gas (type, T, p)

4. Mixture gas adsorption processes:
   Modifications of SGC needed.