



# Diffusion in Zeolites

## Project 2:

### Transient and Equilibrium Measurements of Sorption on Zeolites

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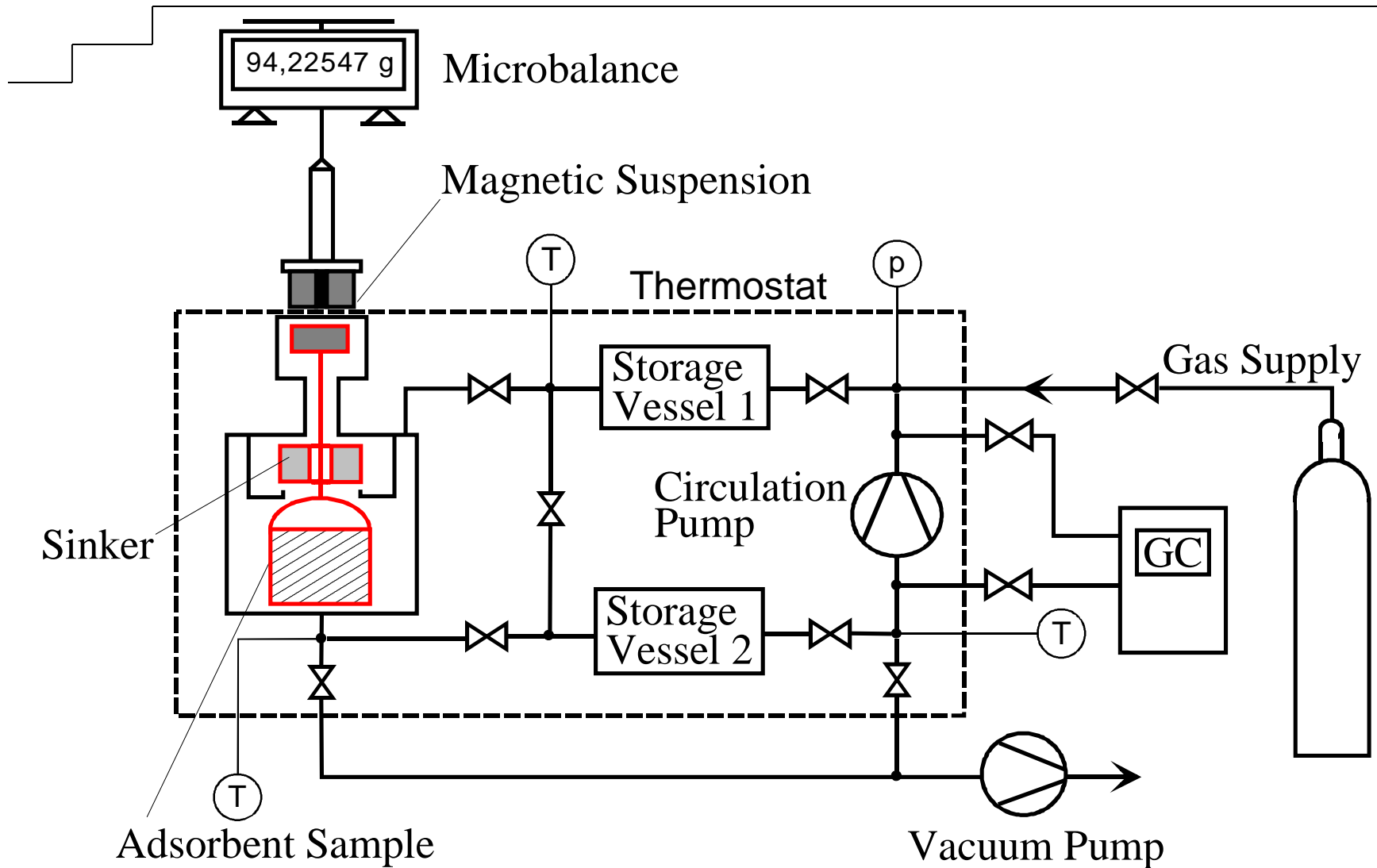
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1. Experimental
2. Kinetic of Adsorption Processes
3. Macroscopic Diffusion Coefficient
4. Gas-Adsorption Equilibria

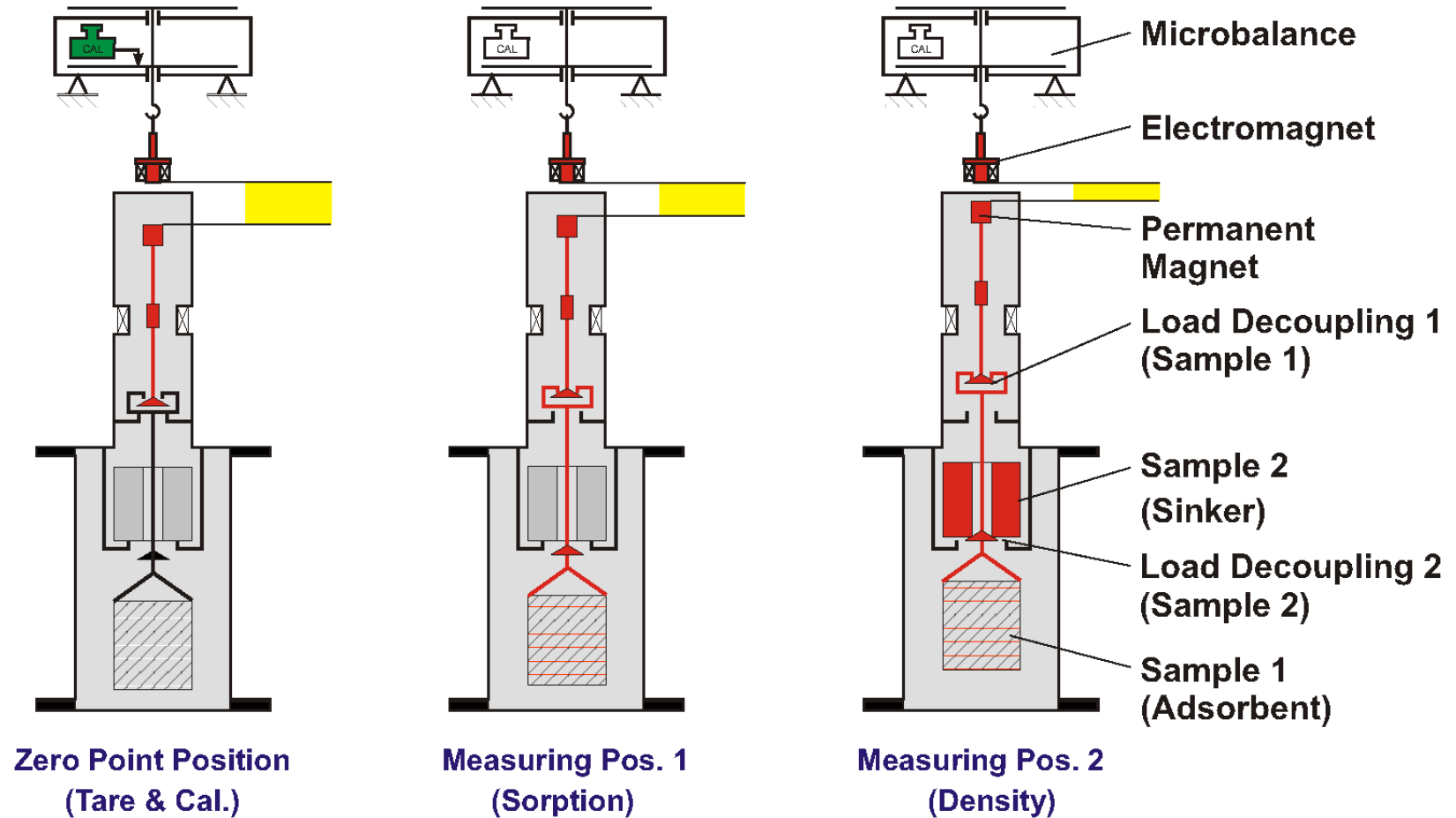
# Gas Adsorption Equilibria

## Measurement Methods

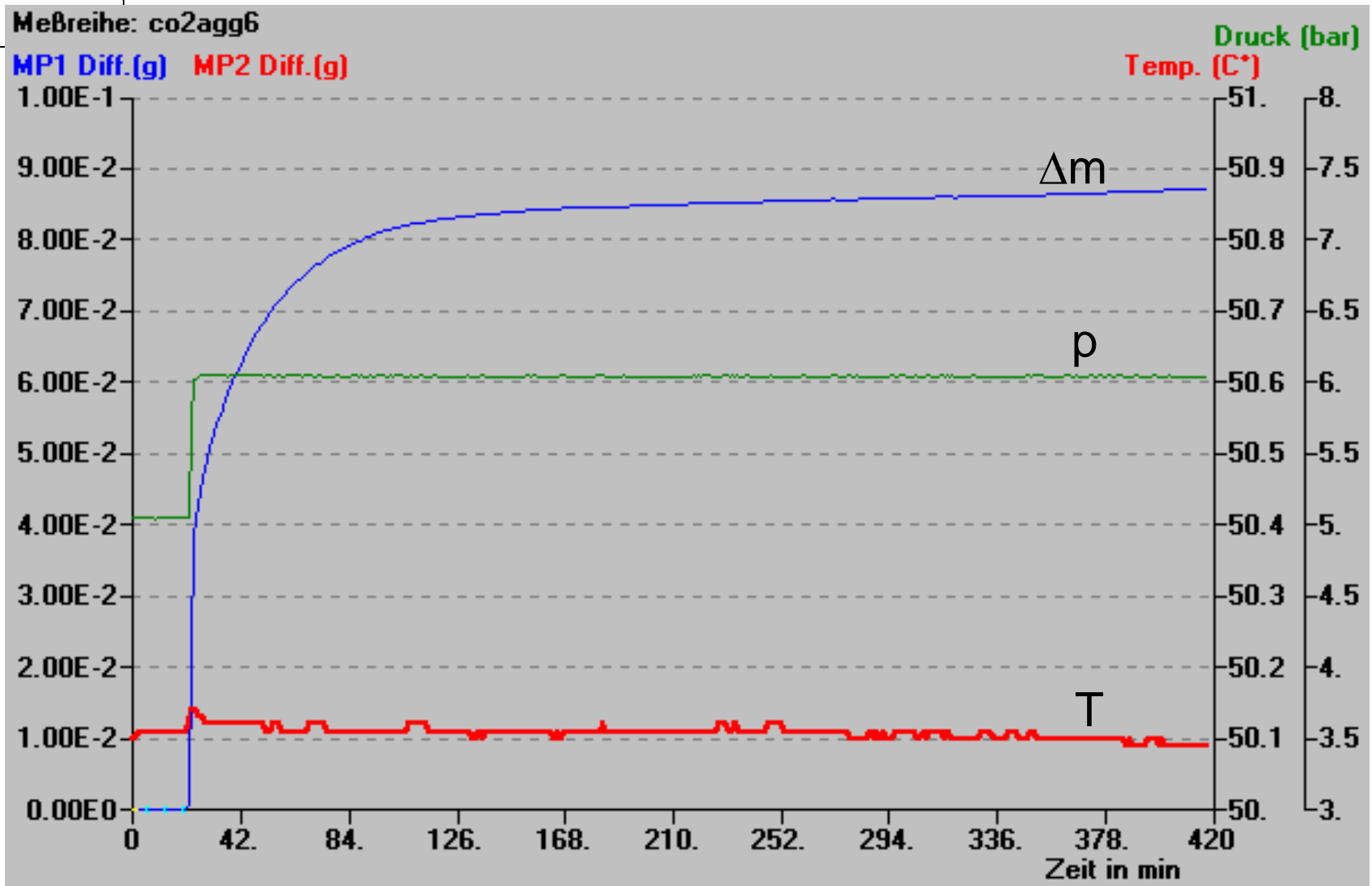
		M	G	O	SP	CHR	D	C
Manometry	(M)		++	+	0	++	++	0
Gravimetry	(G)	2		+	0	+	+	0
Oscillometry	(O)	1, V	1, V		0	0	0	0
Spectroscopy	(SP)	(2)	(2)	1, V		-	-	AMA
Chromatography	(CHR)	$\geq 2$	$\geq 2$	$\geq 2^*$	-		-	-
Densimetry	(D)	2	2	1, V	-	-		-
Calorimetry	(C)	(1)	(1)	(1)	1	-	-	



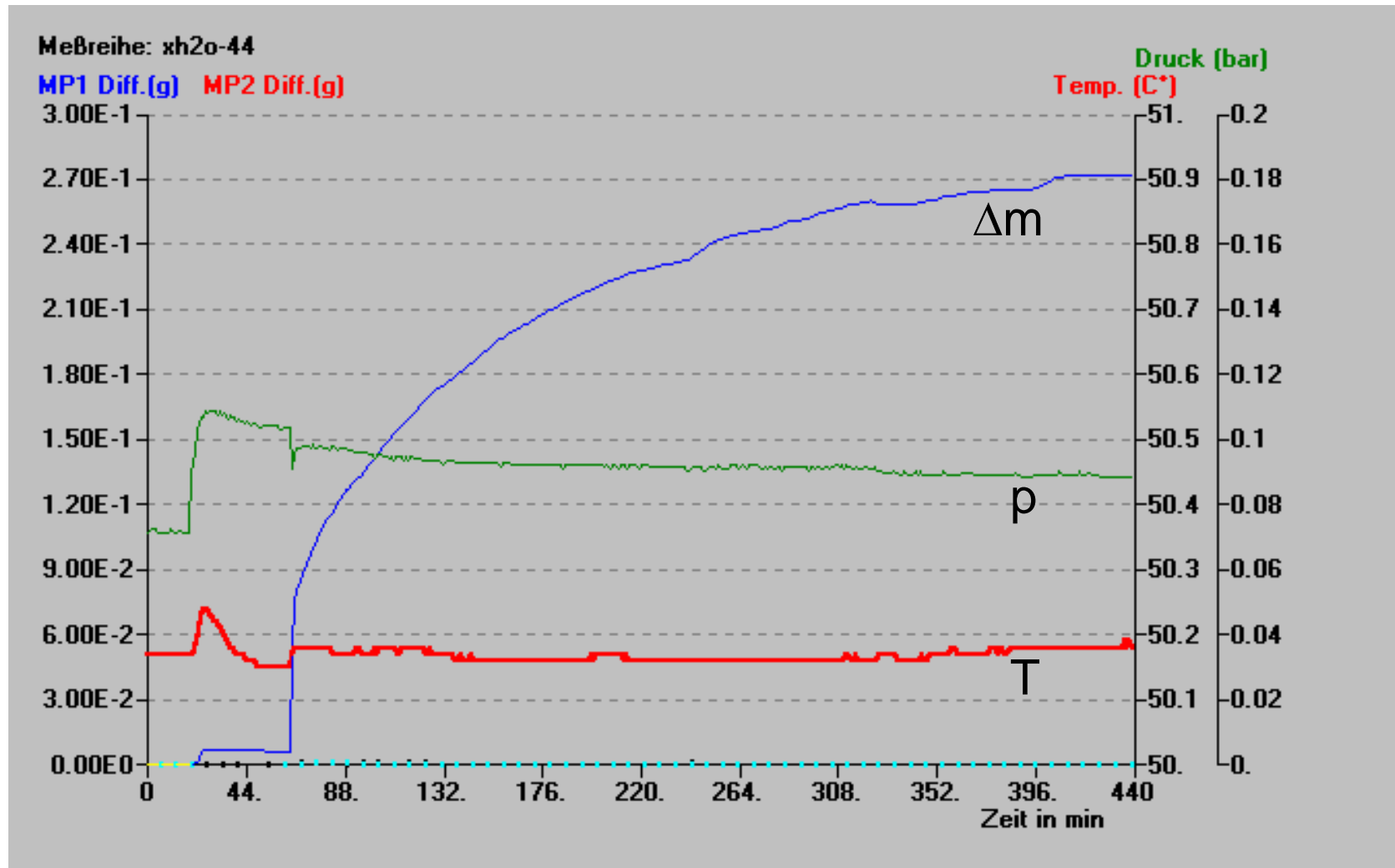
**Instrument for gravimetric measurements of transient adsorption and adsorption equilibria**



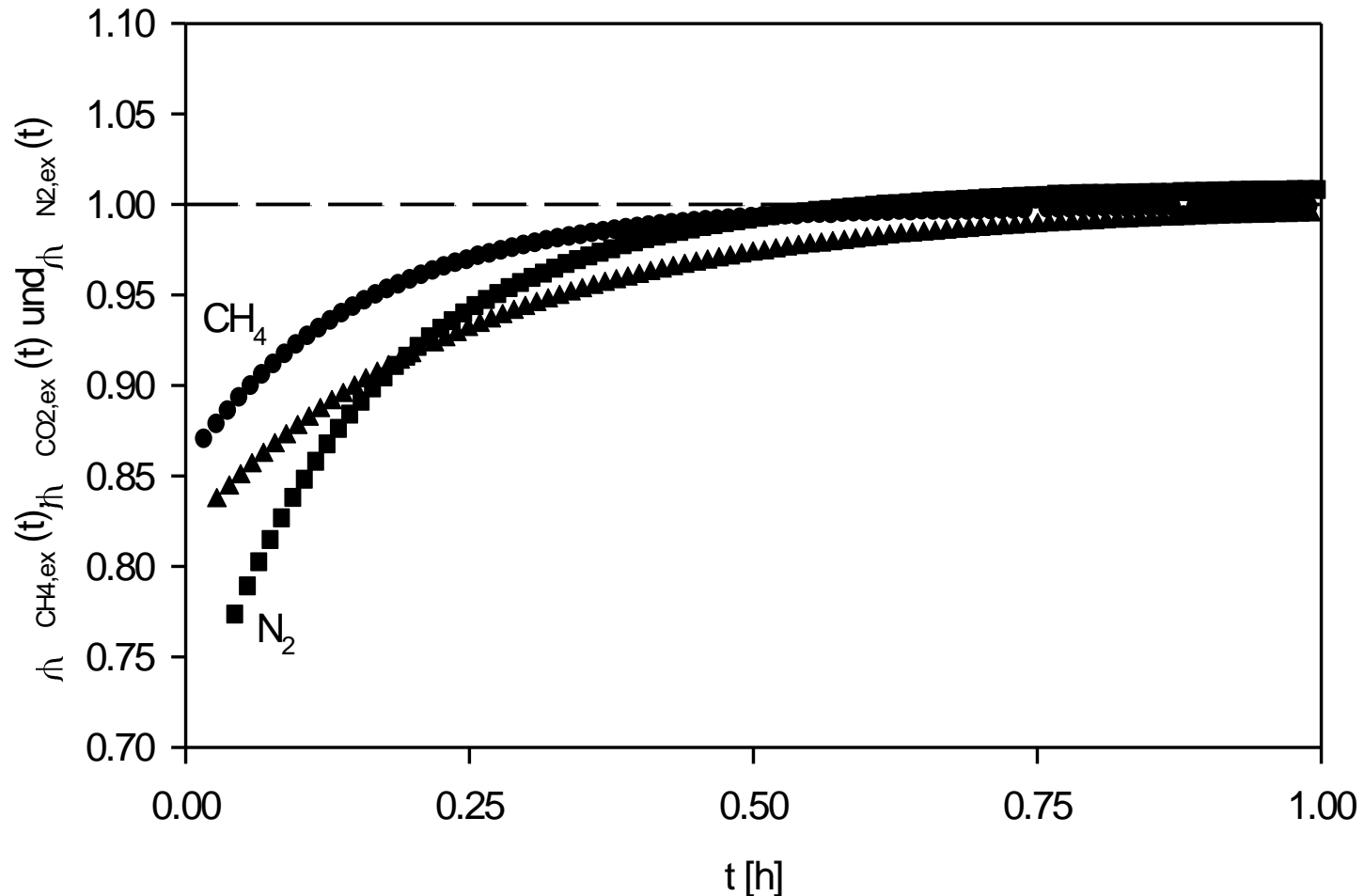
**Dual mode suspension balance. Schematics of working positions.**



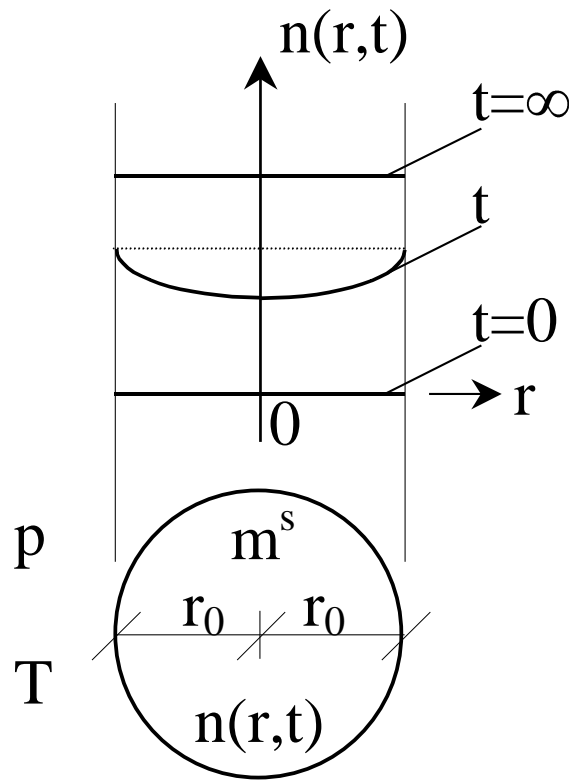
**Measuring record: Sorption of gaseous carbon dioxide on water preloaded molecular sieve Na 13X (56 mg H<sub>2</sub>O/g Na 13X).**



Measuring record: Sorption of H<sub>2</sub>O on Na 13X at T = 50.18 C.



**Relative excess amount adsorbed ( $\Psi_i = n_0(t)/n_i(\infty)$ ) of gases  $i = CH_4$ ,  $CO_2$ ,  $N_2$  on activated carbon Norit R1 at  $T = 298K$ . Equilibrium gas pressure:  $p(CH_4) = 0.64 \text{ bar}$ ,  $p(CO_2) = 0.14 \text{ bar}$ ,  $p(N_2) = 6.3 \text{ bar}$ . Ref.: F. Dreisbach, VDI, Ser. 3, Nr. 547, p. 130, 1998.**



$$n(t) = \int_0^{r_0} n(r,t) dr$$

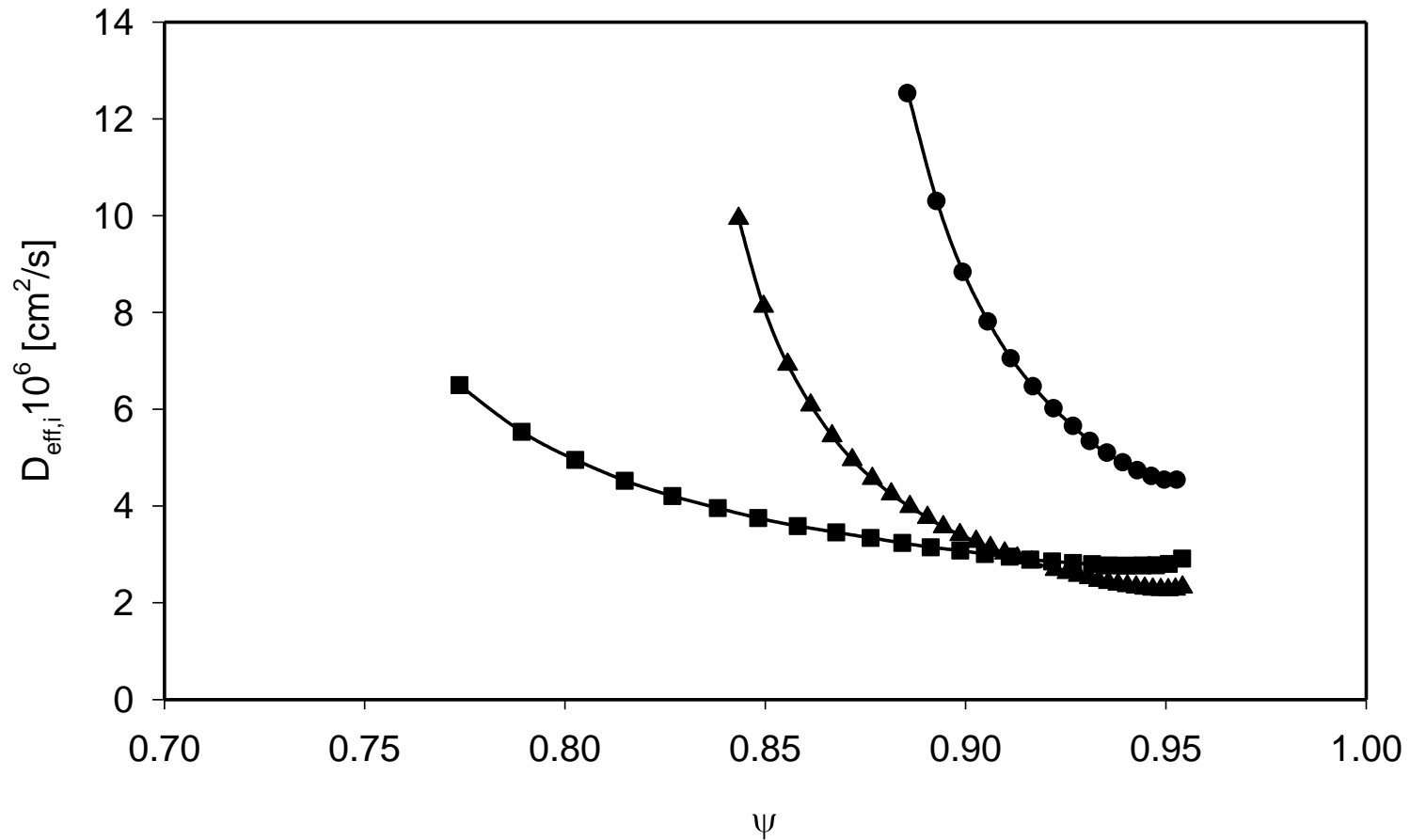
$$\Psi(t) = \frac{n(t)}{n(\infty)}$$

$$\partial_t n(r,t) = D_{\text{eff}} \Psi \Delta n(r,t)$$

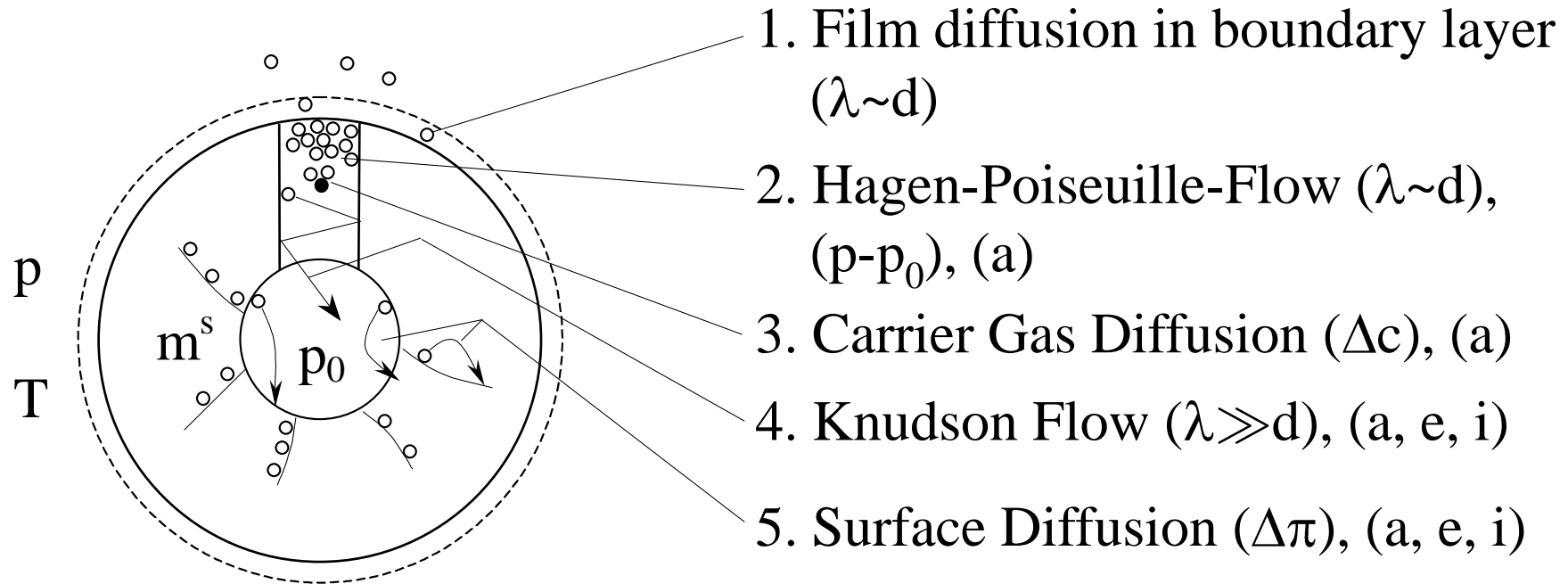
$$D_{\text{eff}} \Psi = \frac{r_0^2}{\pi t \Psi} \left( 1 - \sqrt{1 - \frac{\pi}{3} \Psi} \right)^2$$

**Isothermal mass transfer process from gas (p, T) to sorbent (m<sup>s</sup>).  
Effective or equivalent Diffusivity (D<sub>eff</sub>).**

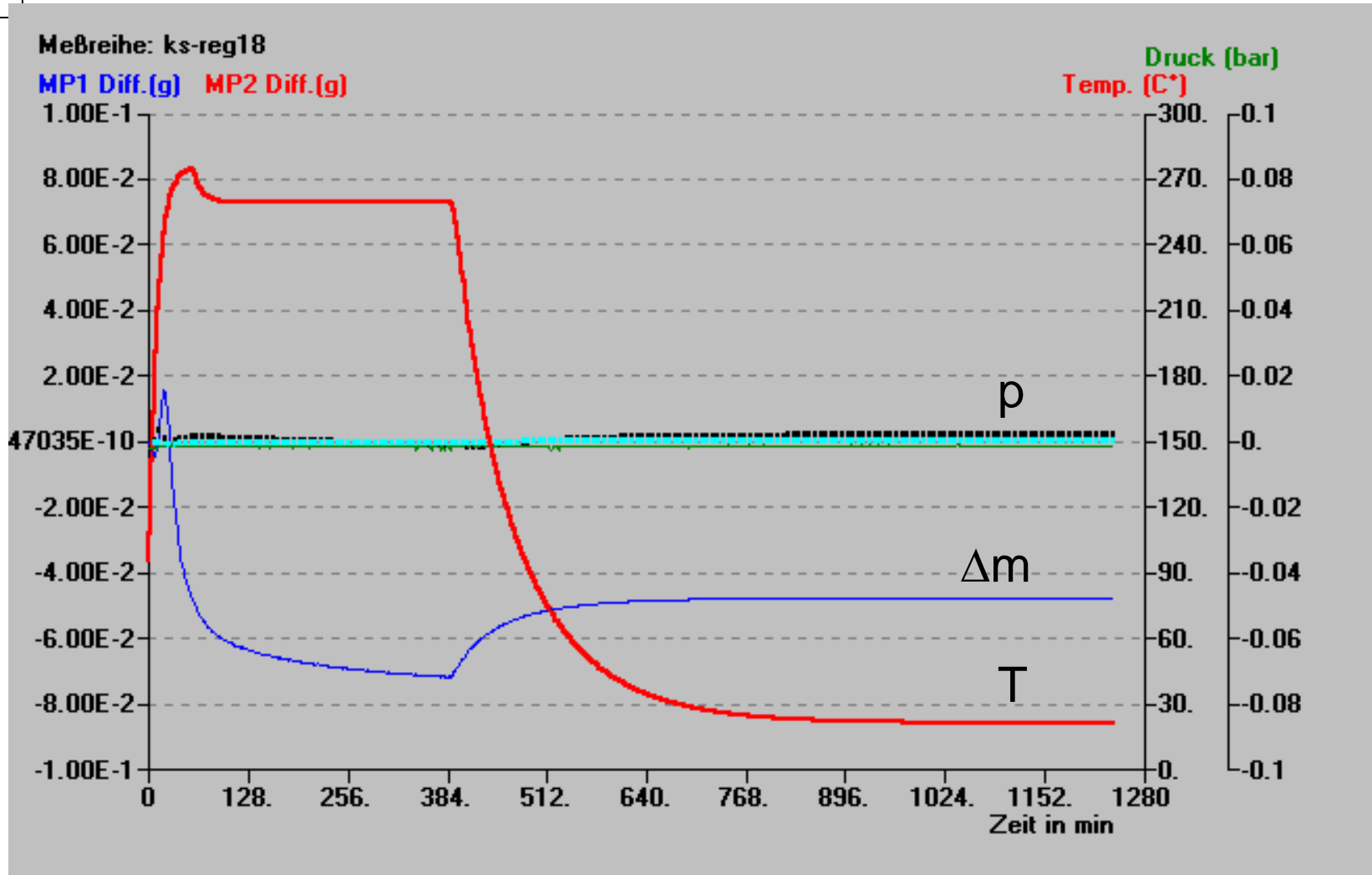




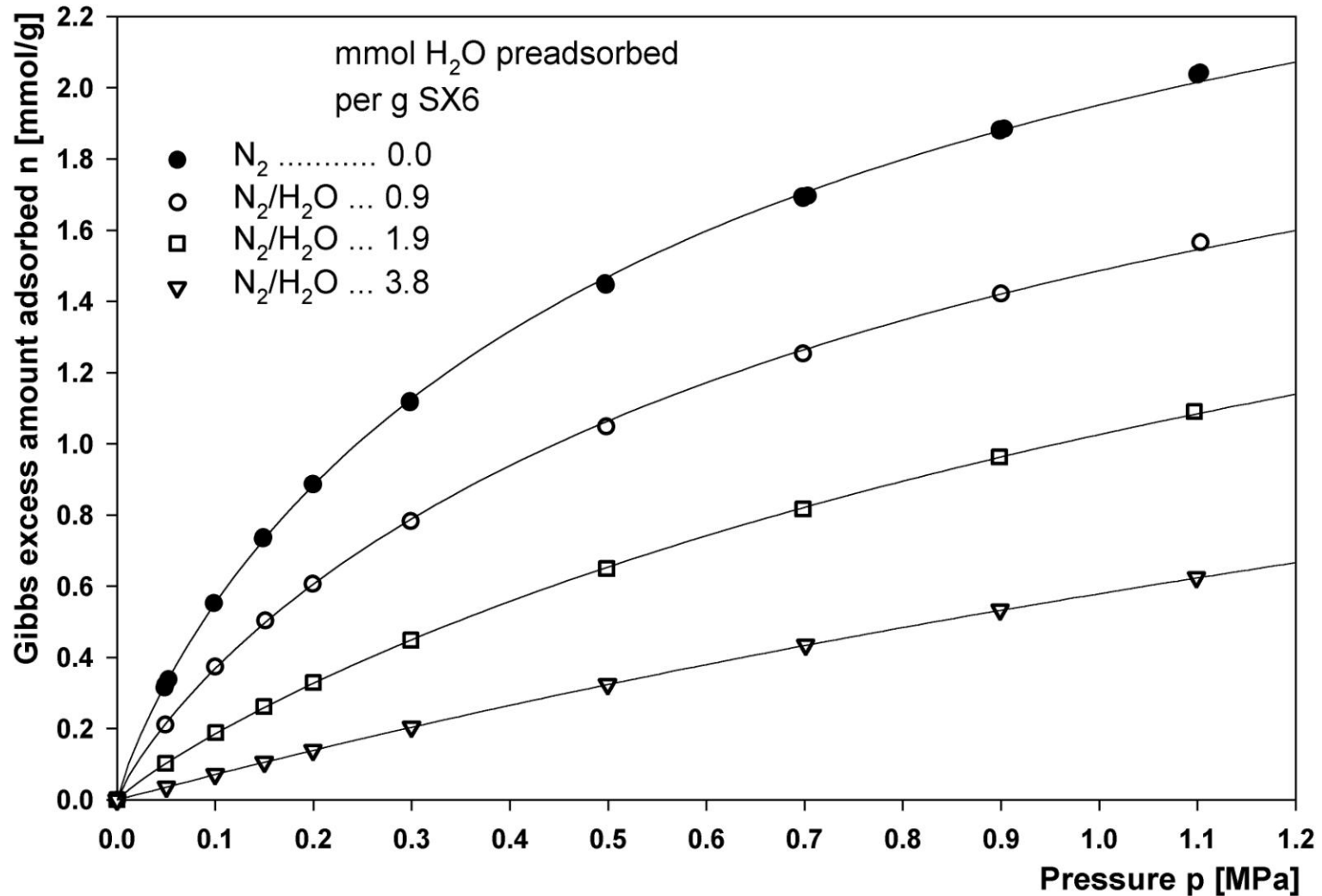
**Effective or equivalent diffusion coefficient ( $D_{\text{eff}}$ ) of gases CH<sub>4</sub> (●), CO<sub>2</sub> (□), N<sub>2</sub> (▲) during isothermal adsorption on activated carbon Norit R1 at T=298K and gas pressures  $p(\text{CH}_4)=0.64\text{bar}$ ,  $p(\text{CO}_2)=0.14\text{bar}$ ,  $p(\text{N}_2)=6.3\text{bar}$ . Ref.: F. Dreisbach, VDI, Ser. 3, Nr. 547, p. 132, 1998.**



**Mass transport mechanisms during pure gas adsorption processes on porous sorbents.**



**Regeneration process of zeolite Köstrolith SX6 in Vacuum during 5h at  $T = 523\text{K}$ .**



**Adsorption isotherms of nitrogen (N<sub>2</sub>) on zeolite Köstrolith SX6 without and with presorbed water of (0.91, 1.88, 3.81) mmol H<sub>2</sub>O / g SX6 at 313 K.**

$$\text{Gravimetry: } \Omega = m^a - \rho^f V^a \quad (1)$$

## Buoyancy correction:

A: Gibbs excess mass

$$V^{\text{as}} = 0 + V_{\text{He}}^{\text{s}} \quad (2A)$$

$$\Omega_{\text{He}} = -\rho^f V_{\text{He}}^{\text{s}} \quad (3)$$

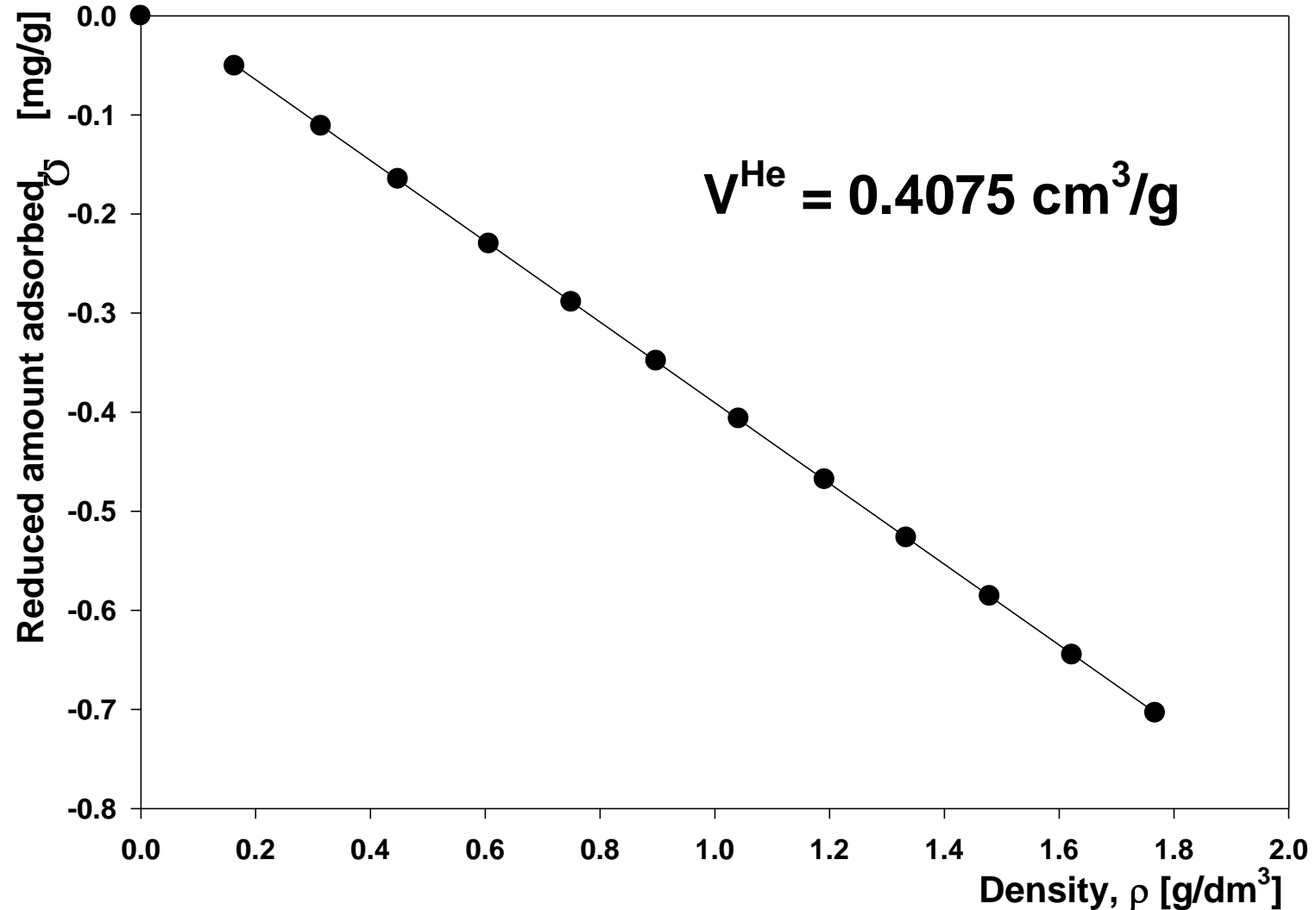
$$(1, 2A) \quad \underline{m_{\text{GE}}^a} = \Omega + \rho^f V_{\text{He}}^{\text{s}} \quad (4)$$

B: Absolute mass adsorbed

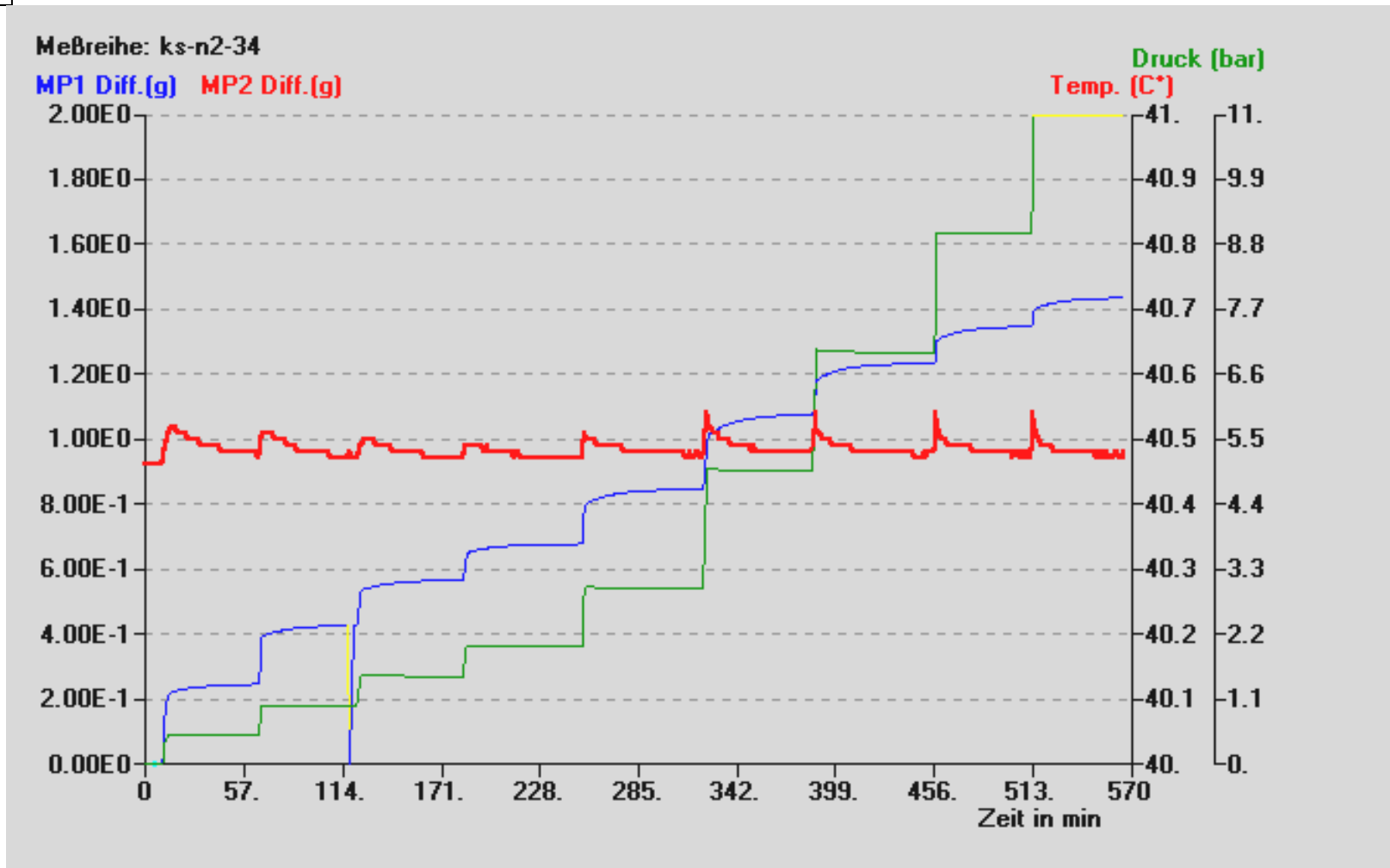
$$V^{\text{as}} = \frac{m^a}{\rho_0^{\text{L}}} + V_{\text{He}}^{\text{s}} \quad (2B)$$

$$m^a = \frac{\Omega + \rho^f V_{\text{He}}^{\text{s}}}{1 - \rho^f / \rho_0^{\text{L}}}$$

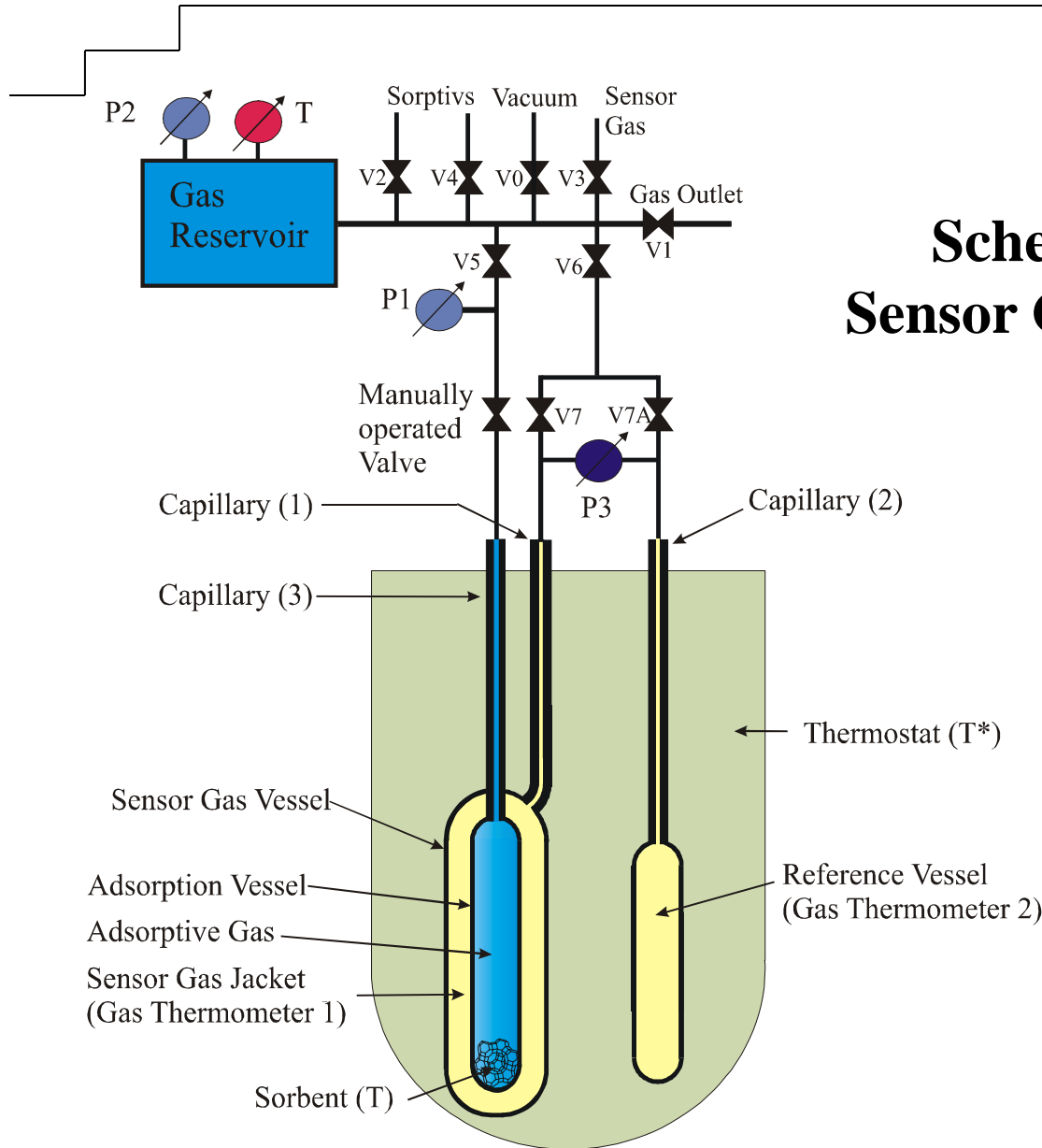
$$(1, 2B) \quad \underline{m^a} = \frac{m_{\text{GE}}^a}{1 - \rho^f / \rho_0^{\text{L}}} \cong m_{\text{GE}}^a \quad \rho^f \rightarrow 0$$



**Measured adsorption equilibria of pure Helium on molecular sieve (Na 13X, Linde AG) at T = 323 K.**

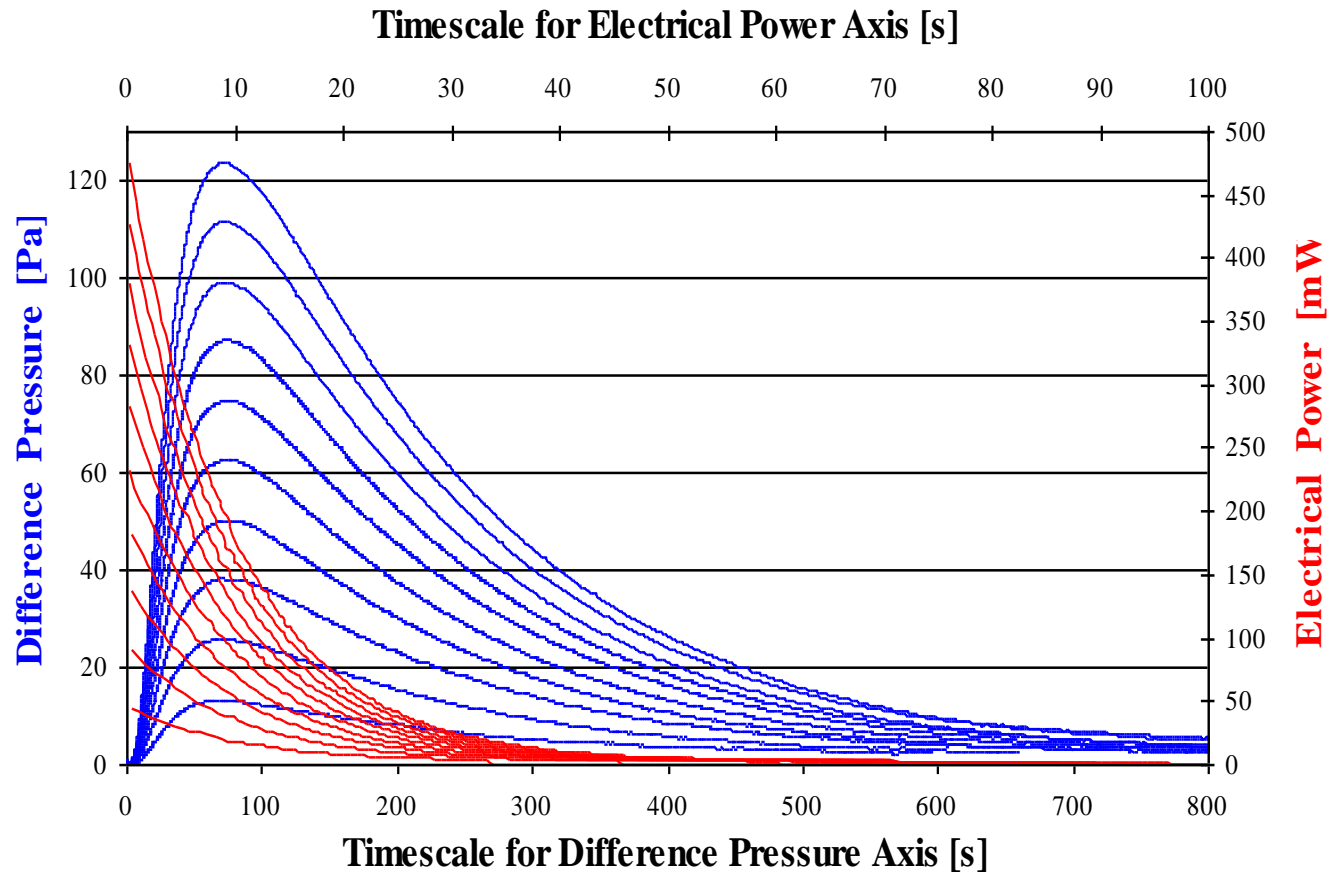


**Adsorption of N<sub>2</sub> in molecular sieve Köstrolith SX6 at T=313.6K**



**Schematic diagram of a  
 Sensor Gas Calorimeter (SGC)**

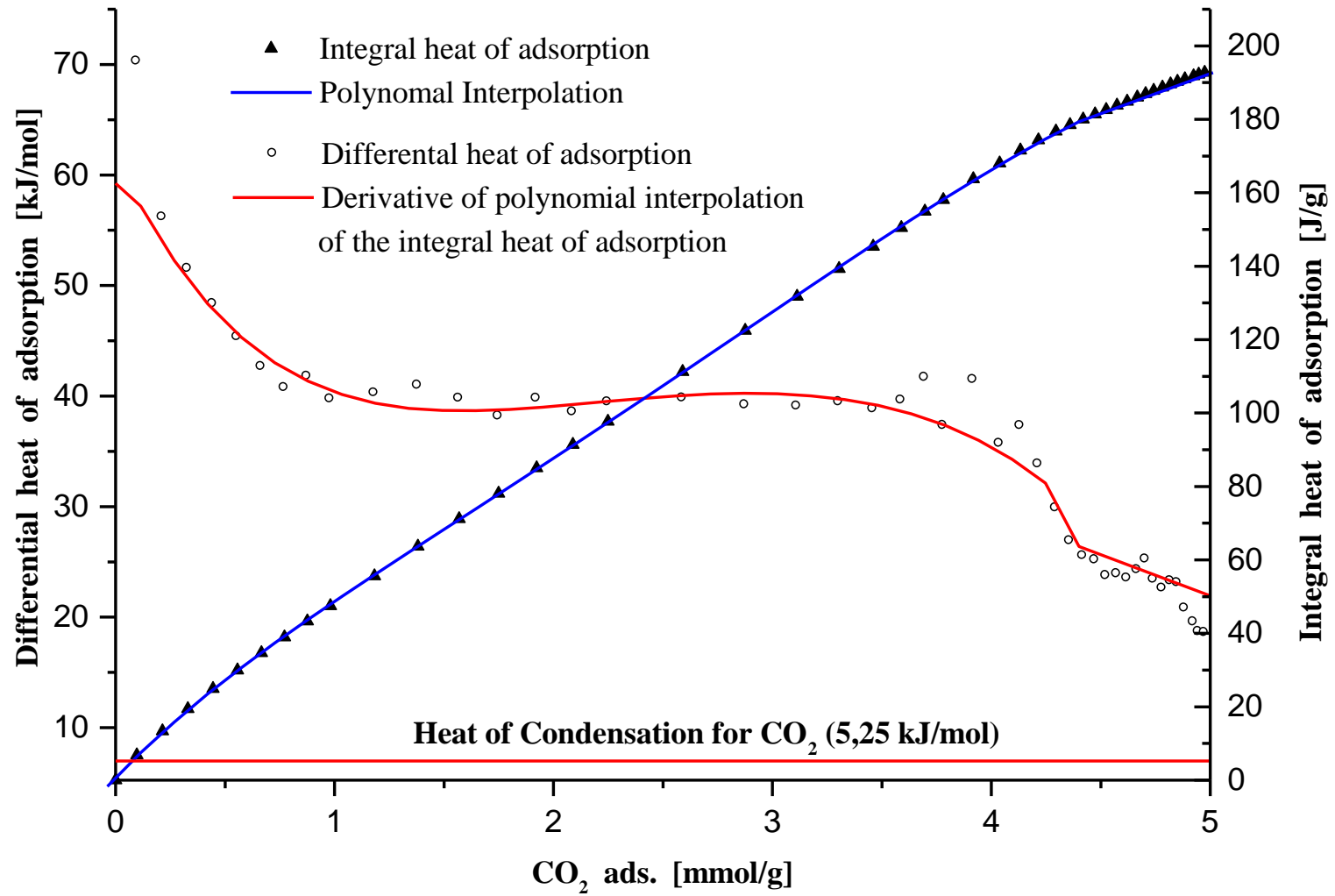




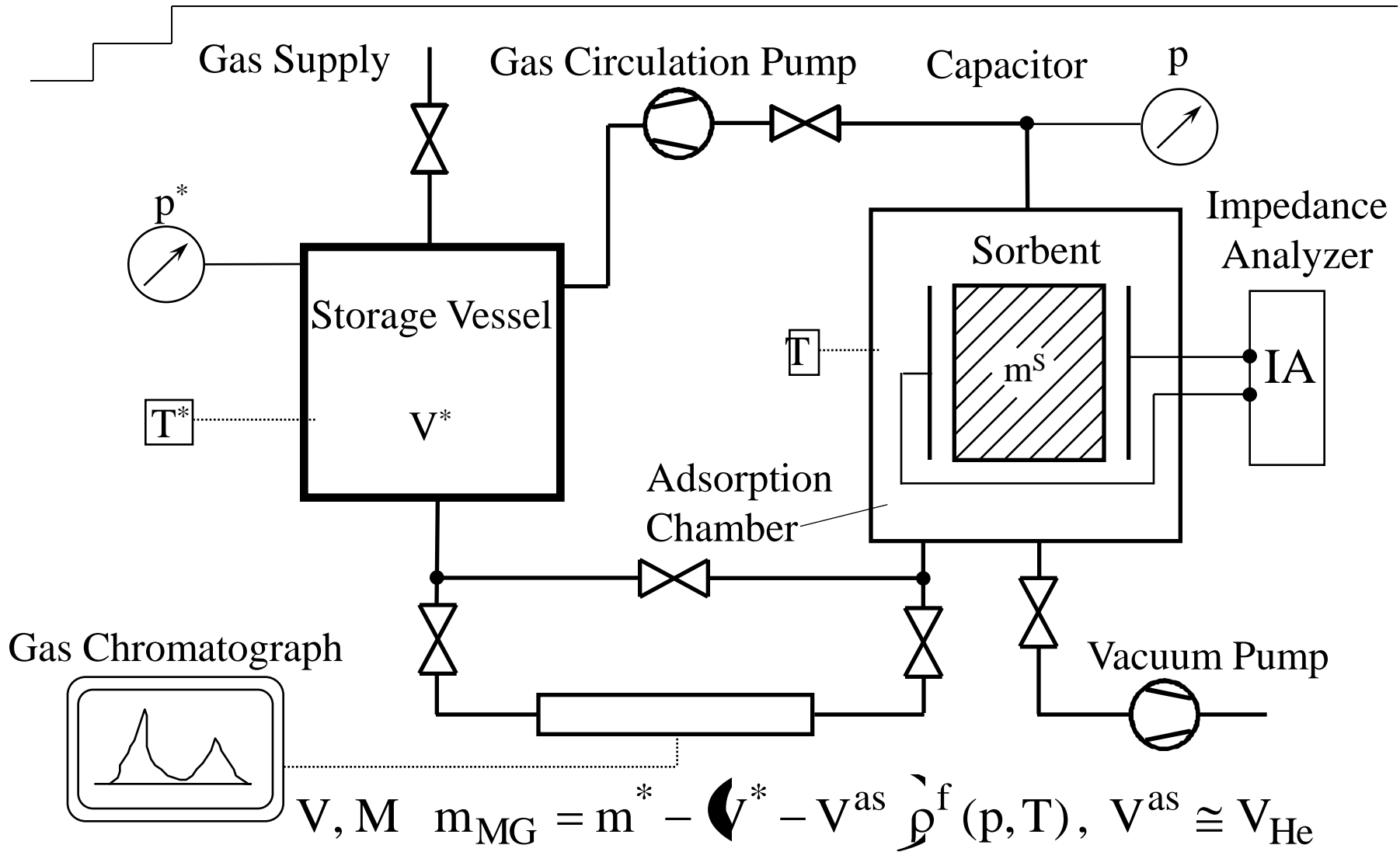
**Calibration experiments in the SGC 0.5J to 5J**

**Sensor gas  $N_2$  (1.6bar),  $T=298K$ ,  $\tau=10s$**

Ohmian heat release (red lines)  $\rightarrow$  Pressure signal (blue lines)



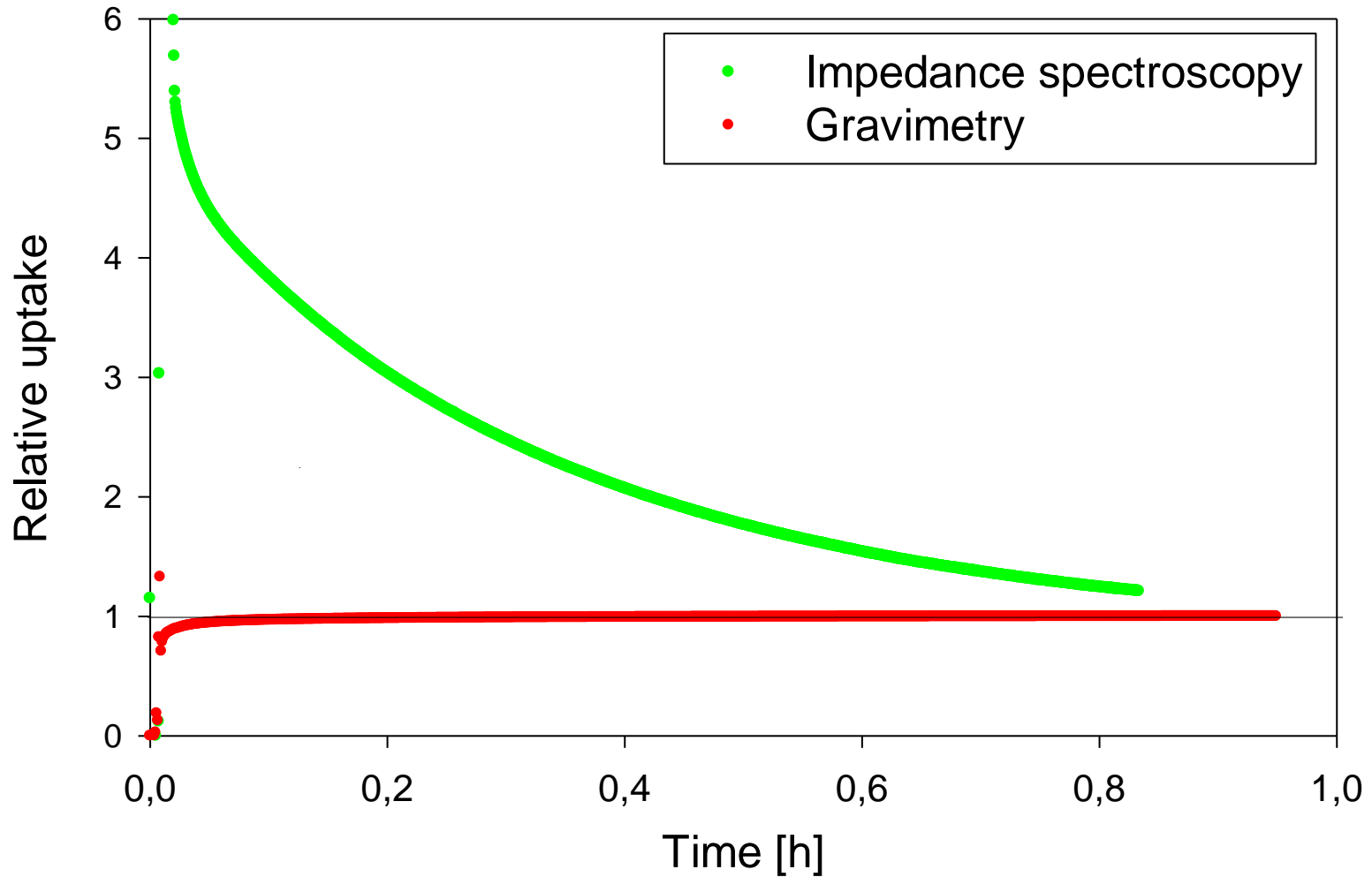
**Heat of adsorption for CO<sub>2</sub> / Na13X, T=298K**



$$V, M \quad m_{MG} = m^* - \rho^f(p, T) (V^* - V^{as}), \quad V^{as} \cong V_{He}$$

$$DE \quad \Omega_{DE} = \alpha(p, T) m_{MG}$$

## Experimental setup for volumetric-dielectric measurements



**Uptake curves of H<sub>2</sub>S on MS 13X, T=298K**