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Investigation of Adsorption Equilibria of Pure Gases (CO, CO_2, CH_4) and their Binary and Ternary Mixtures at T=293K for pressures p✂1.1MPa on Industrial Activated Carbon (ACAL)

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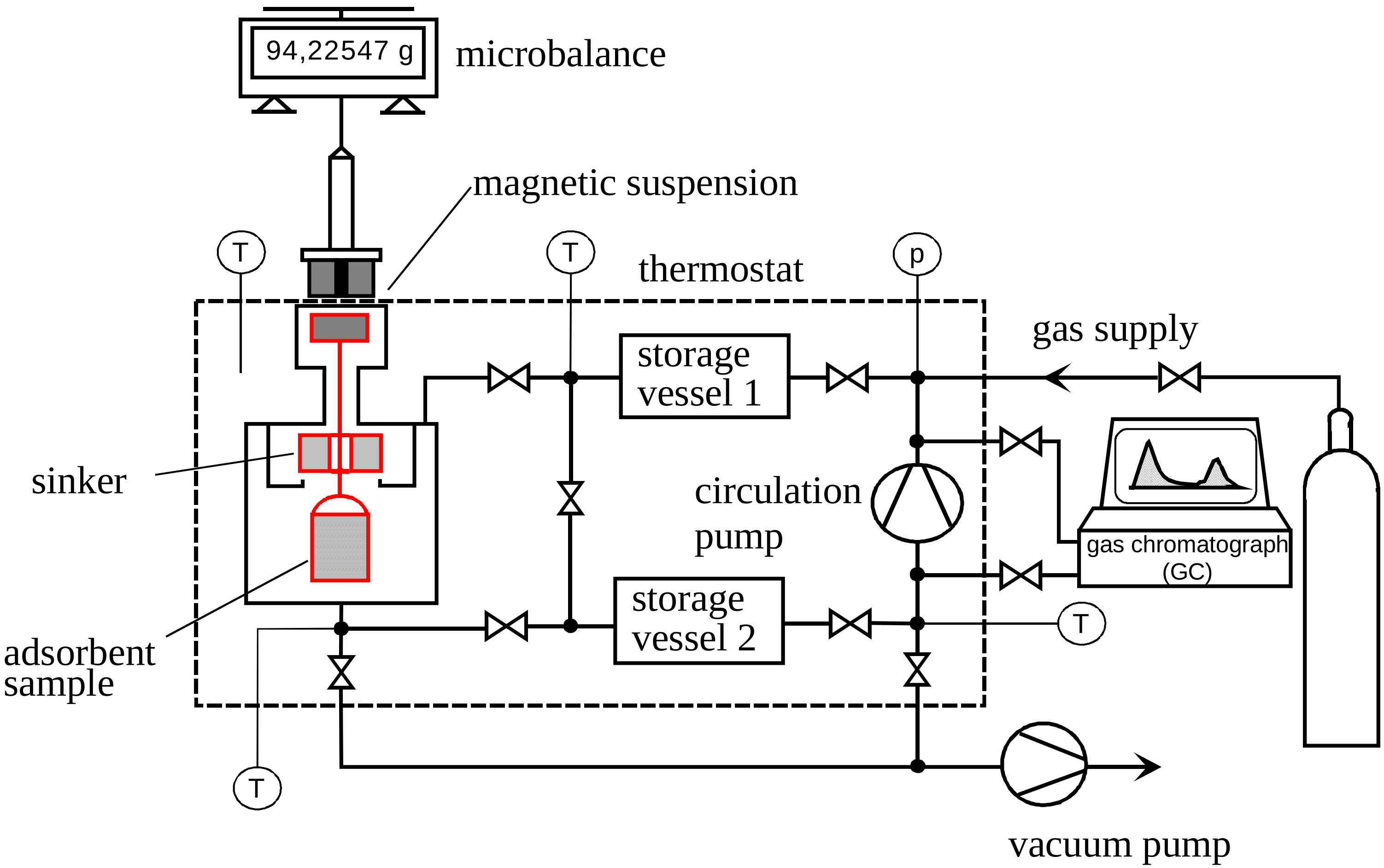
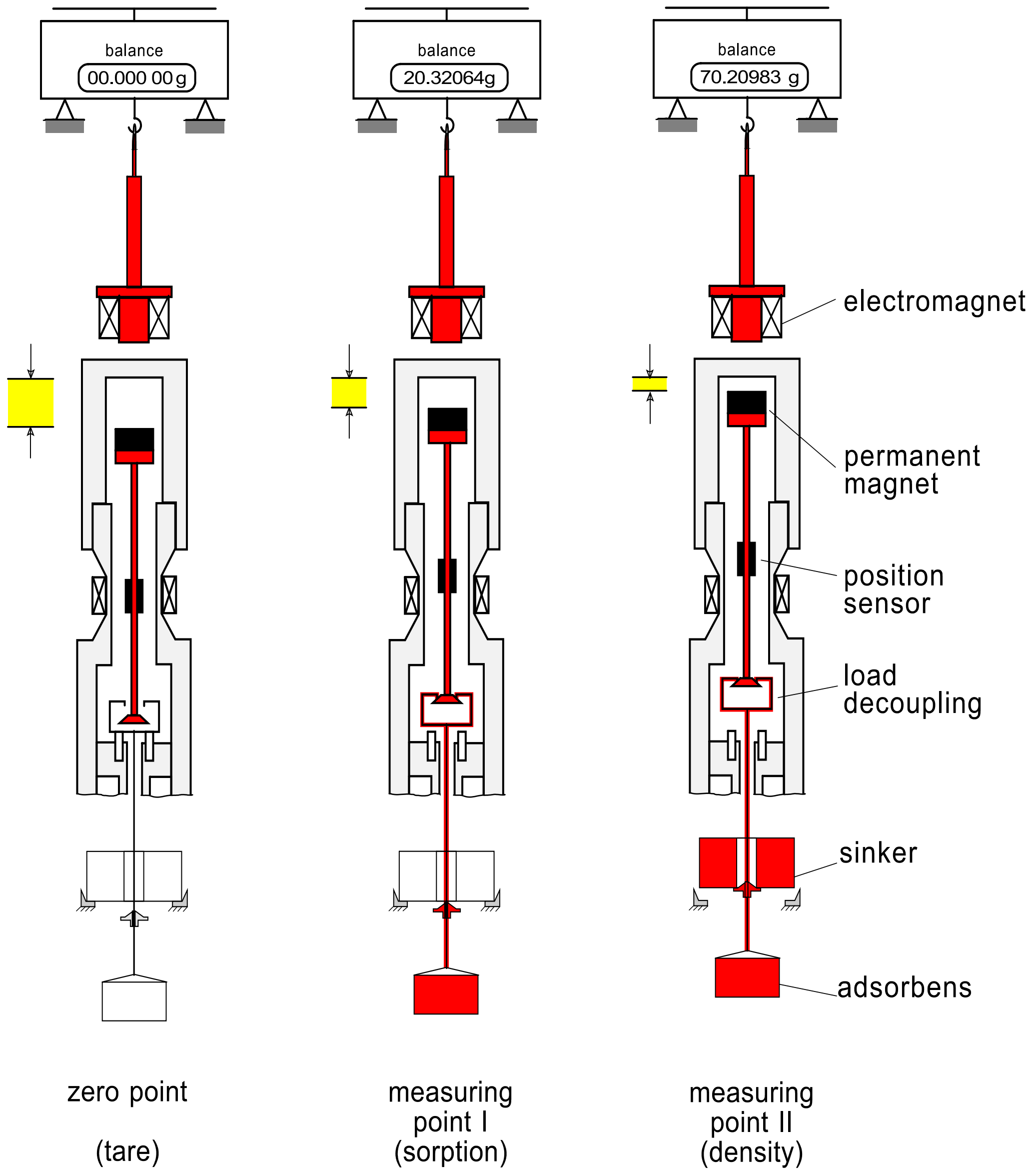


CO, CO_2, CH_4

T = 293K

p = 0 … 1.1MPa

Instrument for volumetric-gravimetric-chromatographic measurements including a magnetic suspension balance (Rubotherm, Germany).



Simultaneous Sorption and Density Mesurement (Rubotherm).

Mass balances

$$m_i^{*} = m_i^{f} + \left(1 + \frac{m_0^{s}}{m^{s}}\right) m_i \qquad i = 1, 2$$

Micro-balance equation

$$\Omega = m_1 + m_2 - V^{as} \frac{m_1^{f} + m_2^{f}}{V^{*} + V^{f}}$$

Adsorptive's equation of state

$$\frac{m_1^{f}}{M_1} + \frac{m_2^{f}}{M_2} = \frac{p \;\; V^{*} + V^{f}}{Z R T}$$

$$M_1 \neq M_2 \;\; \longrightarrow \;\; m_1, m_2, m_1^{f}, m_2^{f} \ldots V^{f} = V - \left(1 + \frac{m_0^{s}}{m^{s}}\right) V^{as}$$

Volumetric-Gravimetric Measurements of Binary Coadsorption Equilibria (Theory)

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Gravimetry

$$\Omega = m - \rho^{f} \cdot V^{as}$$

Buoyancy

A: $V^{as} = V^{s} \cong V^{He} = \text{const.}$ $\qquad m_{ex} = \Omega + \rho^{f} \cdot V^{He}$

B: $V^{as} = V^{s} + V^{a} \cong V^{He} + \dfrac{m}{\rho^{liquid}}$ $\qquad m = \dfrac{\Omega + \rho^{f} \cdot V^{He}}{1 - \dfrac{\rho^{f}}{\rho^{liquid}}} = \dfrac{m_{ex}}{1 - \dfrac{\rho^{f}}{\rho^{liquid}}}$

with $\rho^{liquid} \triangleq$ sorptive's liquid density at reference pressure (p=0.1MPa).

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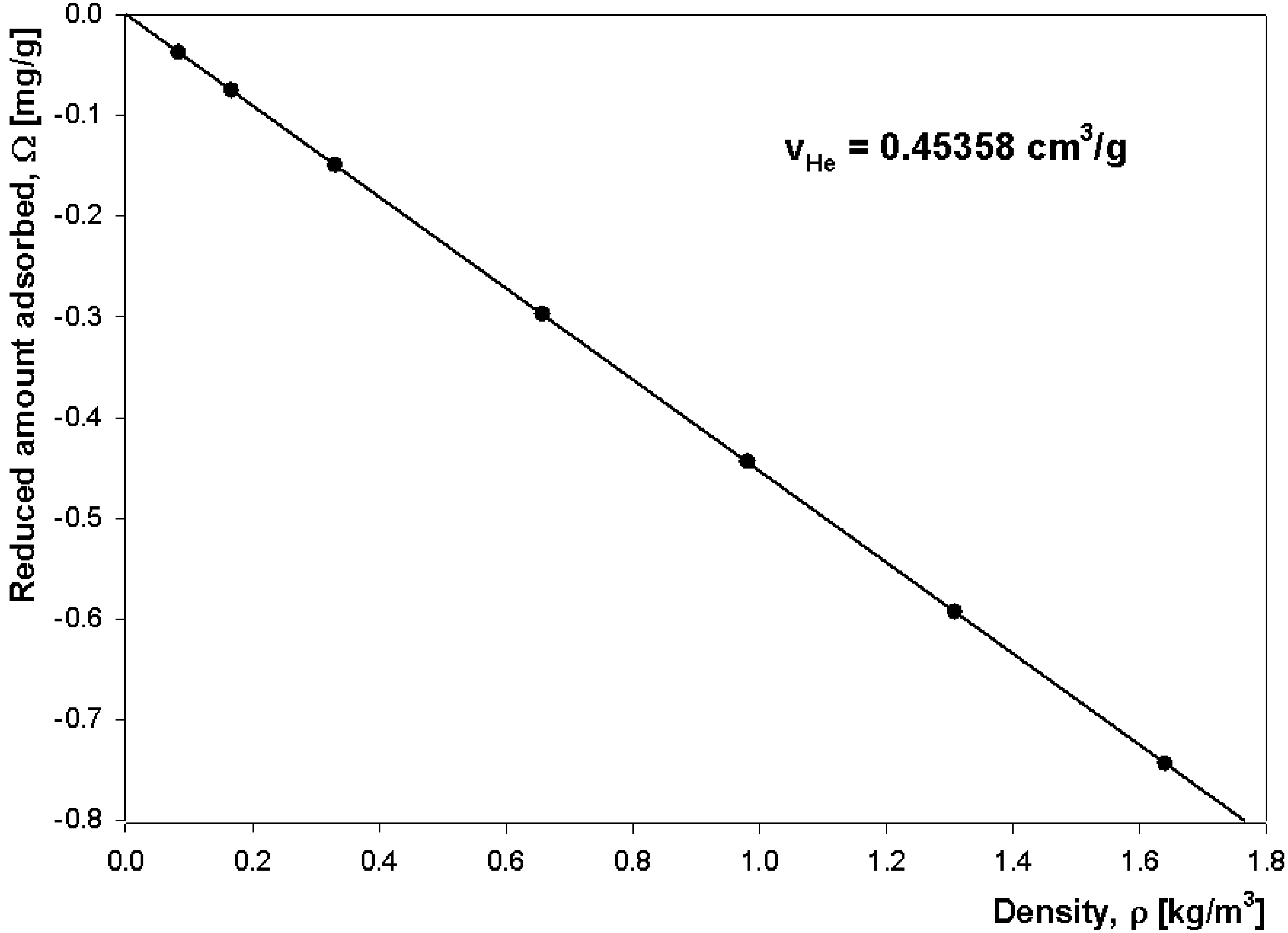

Adsorption isotherm of helium (He) on industrial activated carbon (ACAL) at 293K.

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Data Correlation and Prediction of Mixture Adsorption: Generalized two-site (Dual-Place) AI (2LAI)

For pure gases:

$$n(p,T) = n_\infty^P(T) \cdot \alpha^P \cdot \frac{(b^P(T) \cdot p)^{\alpha^P}}{1 + (b^P(T) \cdot p)^{\alpha^P}} + n_\infty^S(T) \cdot \alpha^S \cdot \frac{(b^S(T) \cdot p)^{\alpha^S}}{1 + (b^S(T) \cdot p)^{\alpha^S}}$$

For mixtures:

$$n_i(p,T) = n_{\infty,i}^P(T) \cdot \alpha_i^P \cdot \frac{(b_i^P(T) \cdot p_i)^{\alpha_i^P}}{1 + \sum_i (b_i^P(T) \cdot p_i)^{\alpha_i^P}} +$$

$$n_{\infty,i}^S(T) \cdot \alpha_i^S \cdot \frac{(b_i^S(T) \cdot p_i)^{\alpha_i^S}}{1 + \sum_i (b_i^S(T) \cdot p_i)^{\alpha_i^S}}, \; i = 1,2,3 .$$

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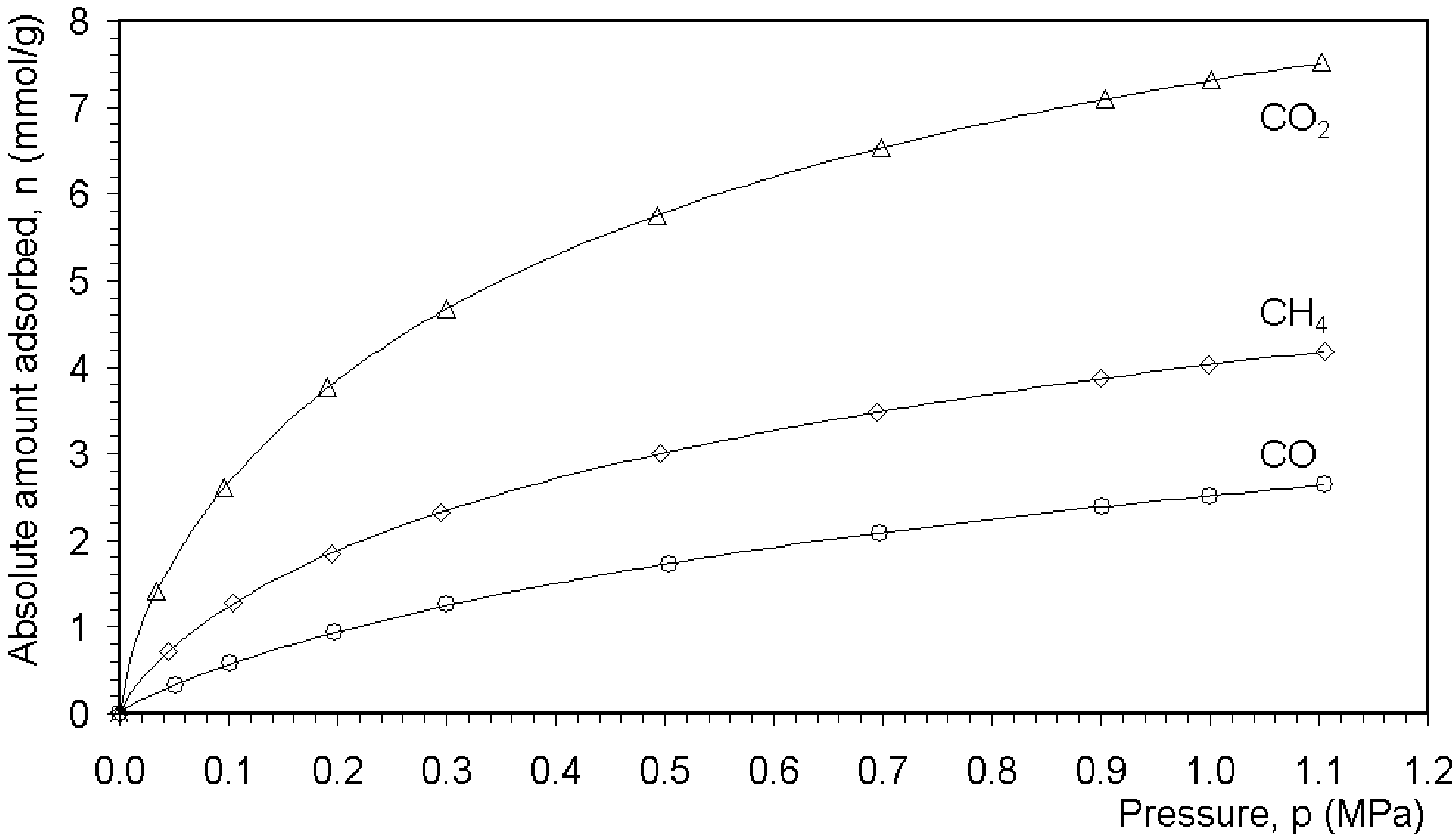

Adsorption equilibria of pure gases CO (○), CH_4 (◇) and CO_2(△) at 293K on industrial activated carbon (ACAL). Datafit: 2LAI (—).

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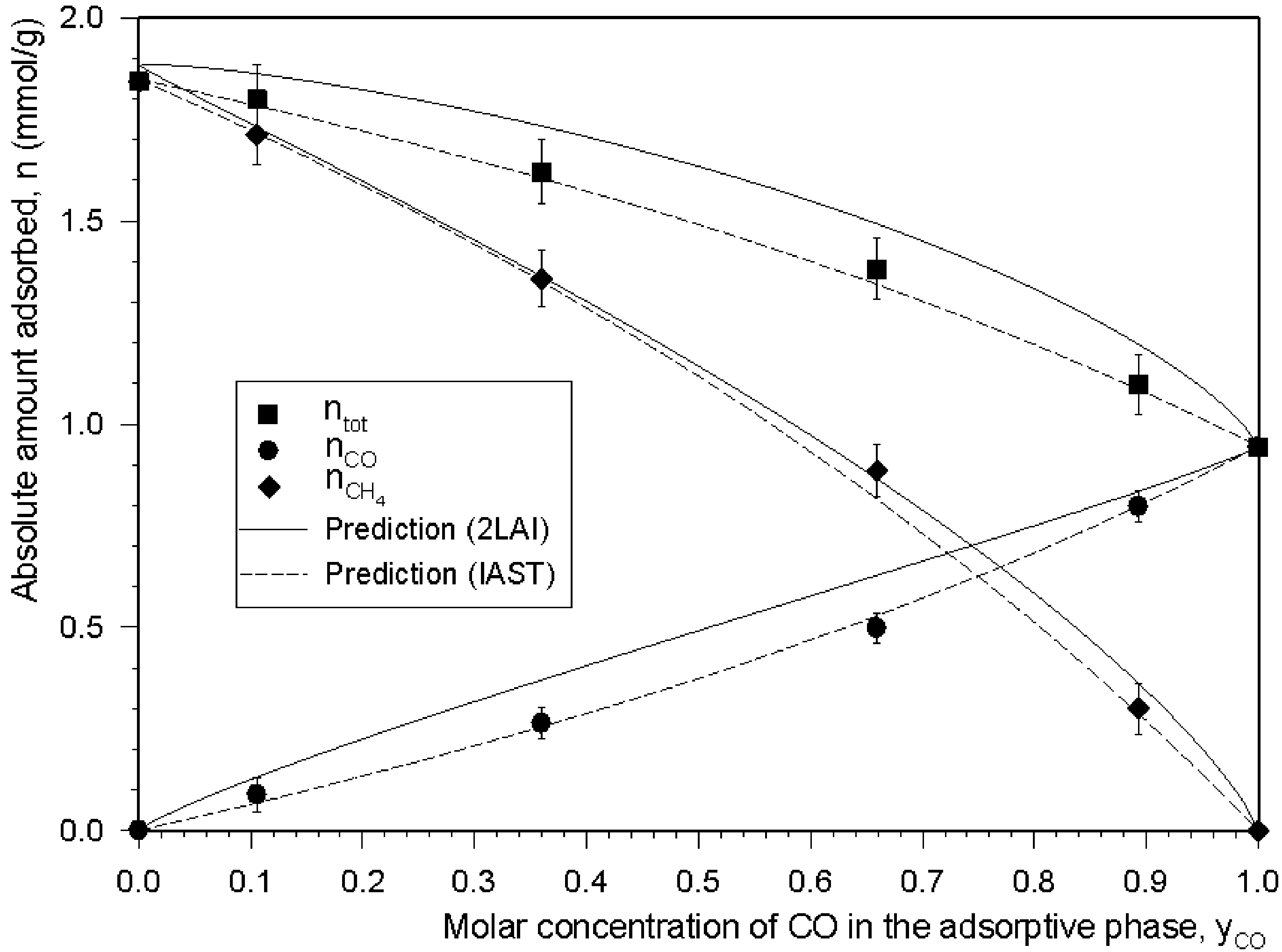

Adsorption equilibria of binary gas mixture CO/CH_4 (n_{tot} (■), partial amount of CO (●), partial amount of CH_4 (◆)) at 293K and 0.2MPa on ACAL. Prediction: 2LAI (—) and IAST (·······).

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CO/CH_4 T=293K ACAL		f_m, σ %			
		x_{CO} (adsorbed phase)	n_{CH4} (partial load)	n_{CO} (partial load)	$n_{tot}= n_{CO} + n_{CH4}$
0.2MPa	2LAI	f_m=24.5 σ =29.0	6.11 10.5	30.6 35.2	6.91 7.22
	IAST	**8.46 11.6**	**3.16 4.39**	**7.86 11.5**	**1.39 1.58**
1.0MPa	2LAI	52.0 76.3	5.01 7.31	62.1 83.3	8.21 8.75
	IAST	**3.55 4.07**	**3.33 3.64**	**3.82 4.51**	**2.67 2.86**

- Relative mean deviation (f_m)

$$f_m = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{\left|n_{PRE} - n_{EXP}\right|}{n_{EXP}}\right)_i$$

- Relative dispersion (σ)

$$\sigma^2 = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{\left(n_{PRE} - n_{EXP}\right)^2}{n_{EXP}^2}\right)_i$$

$N = 1 \ldots 4$

Statistical uncertainties (f_m, σ) of coadsorption data CO/CH_4 on ACAL at 293K and 0.2MPa, 1.0MPa predicted from pure adsorption data by two isotherms.

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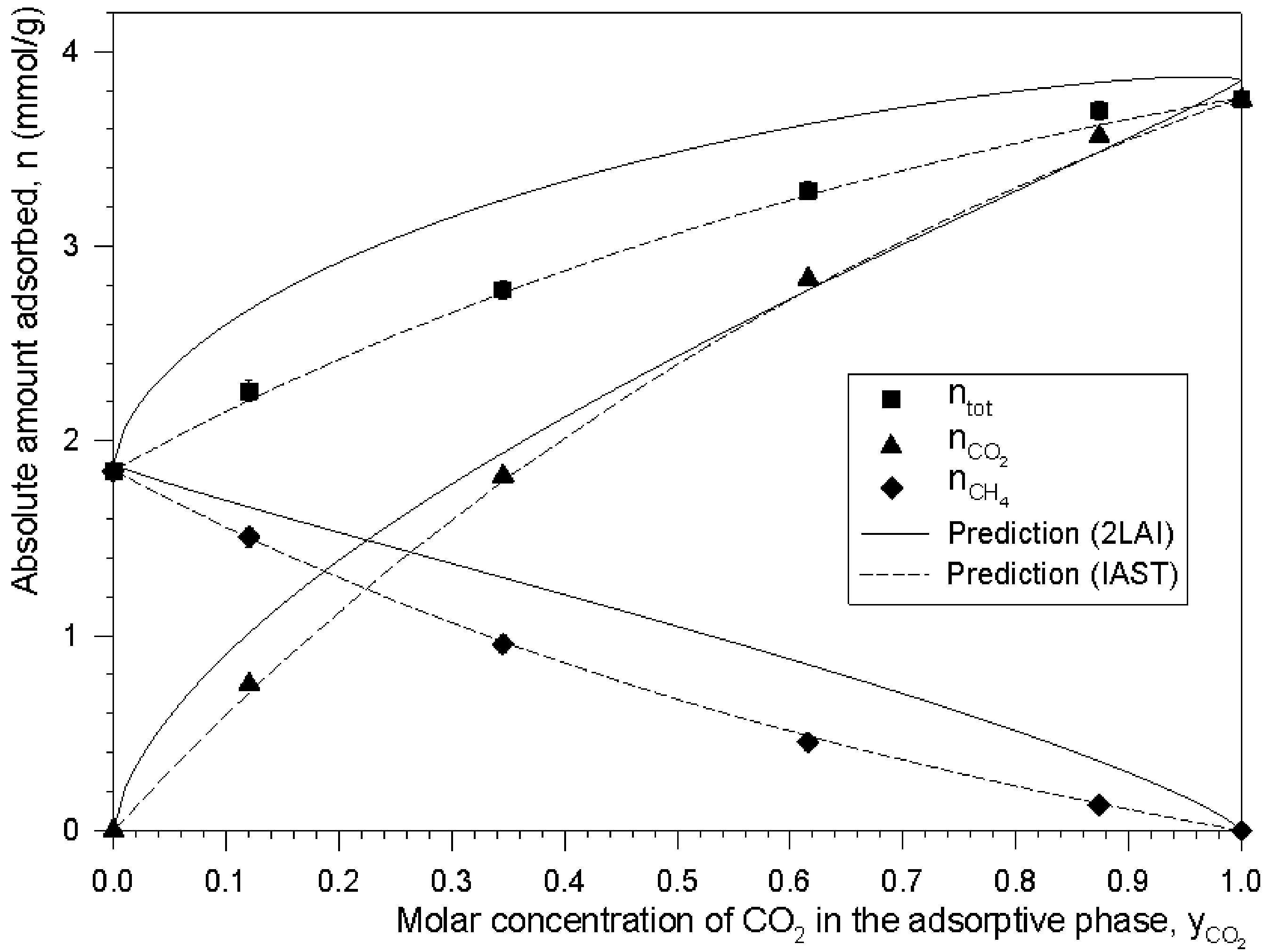

Adsorption equilibria of binary gas mixture CO_2/CH_4 (n_{tot} (■), partial amount of CO_2 (▲), partial amount of CH_4 (◆)) at 293K and 0.2MPa on ACAL. Prediction: 2LAI (—) and IAST (........).

CO_2/CH_4 T=293K ACAL		f_m , σ %			
		x_{CO2} (adsorbed phase)	n_{CO2} (partial load)	n_{CH4} (partial load)	$n_{tot}= n_{CO2} + n_{CH4}$
0.2MPa	2LAI	f_m=9.94 σ =10.4	11.5 17.9	76.3 98.0	12.4 13.7
	IAST	**1.49** **1.97**	**2.78** **3.25**	**3.35** **4.34**	**1.31** **1.50**
1.0MPa	2LAI	12.8 13.2	13.2 18.1	144 196	9.70 11.8
	IAST	**2.09** **2.61**	**6.25** **7.00**	**21.5** **26.3**	**6.08** **6.48**

- Relative mean deviation (f_m)

$$f_m = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{|n_{PRE} - n_{EXP}|}{n_{EXP}}\right)_i$$

- Relative dispersion (σ)

$$\sigma^2 = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{n_{PRE} - n_{EXP}}{n_{EXP}^2}\right)_i^2$$

$$N = 1 \ldots 4$$

Statistical uncertainties (f_m, σ) of coadsorption data CO_2/CH_4 on ACAL at 293K and 0.2MPa, 1.0MPa predicted from pure adsorption data by two isotherms.

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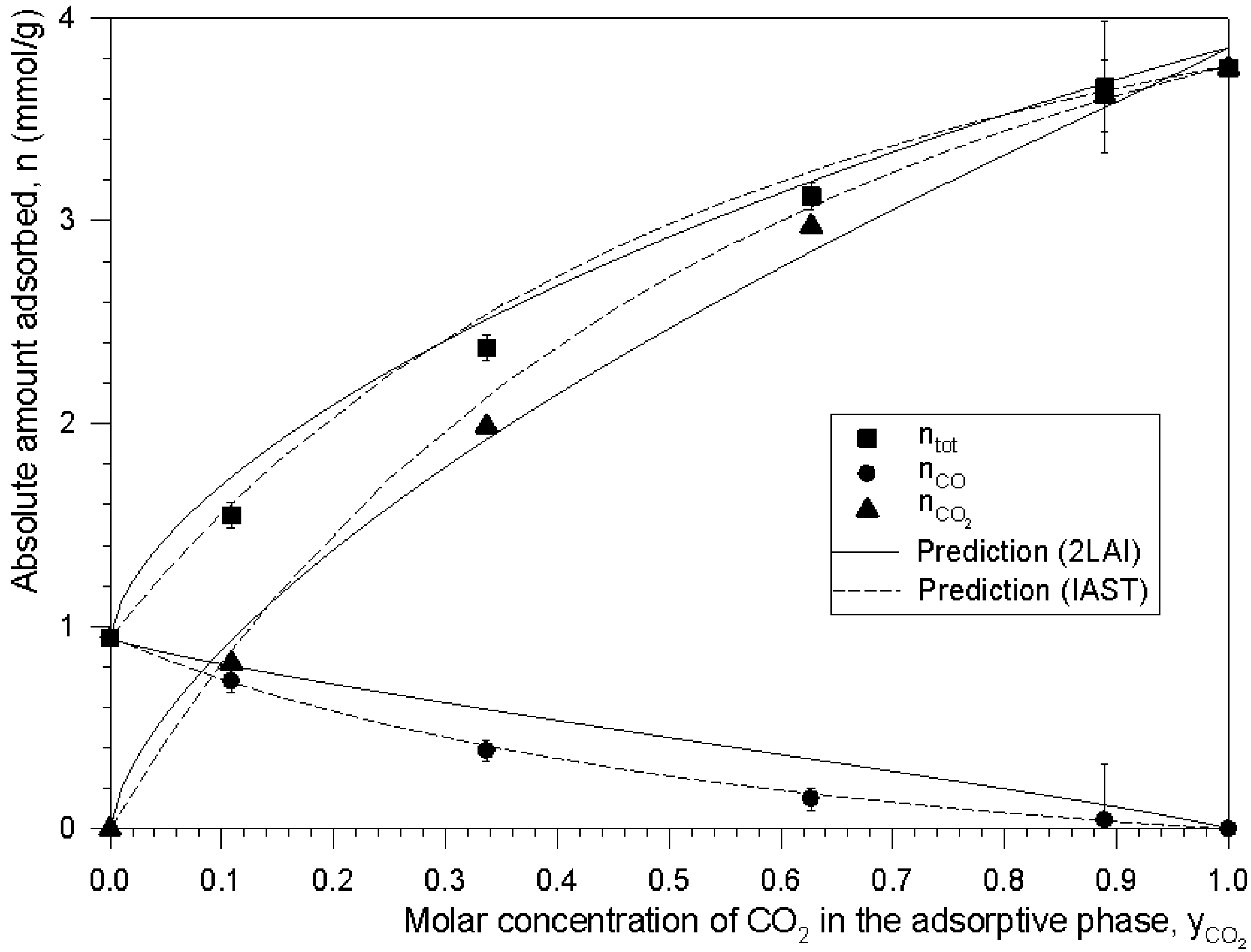

Adsorption equilibria of binary gas mixture CO_2/CO (n_{tot} (■), partial amount of CO_2 (▲), partial amount of CO (●)) at 293K and 0.2MPa on ACAL. Prediction: 2LAI (—) and IAST (⋯⋯).

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CO_2/CO T=293K ACAL		f_m , σ %			
		x_{CO2} (adsorbed phase)	n_{CO2} (partial load)	n_{CO} (partial load)	$n_{tot} = n_{CO2} + n_{CO}$
0.2MPa	2LAI	f_m=6.21 σ =6.57	5.67 7.41	101 130	**3.43** **3.80**
	IAST	**1.16** **1.91**	**4.68** **5.55**	**7.14** **9.21**	**3.82** **4.49**
1.0MPa	2LAI	6.76 7.99	**7.20** **7.99**	219 292	**2.45** **3.20**
	IAST	**0.51** **0.69**	10.1 11.1	**15.6** **19.7**	9.95 10.8

- Relative mean deviation (f_m)

$$f_m = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{\left|n_{PRE} - n_{EXP}\right|}{n_{EXP}}\right)_i$$

- Relative dispersion (σ)

$$\sigma^2 = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{n_{PRE} - n_{EXP}}{n_{EXP}^2}\right)_i^2$$

$N = 1 \ldots 4$

Statistical uncertainties (f_m, σ) of coadsorption data CO_2/CO on ACAL at 293K and 0.2MPa, 1.0MPa predicted from pure adsorption data by two isotherms.

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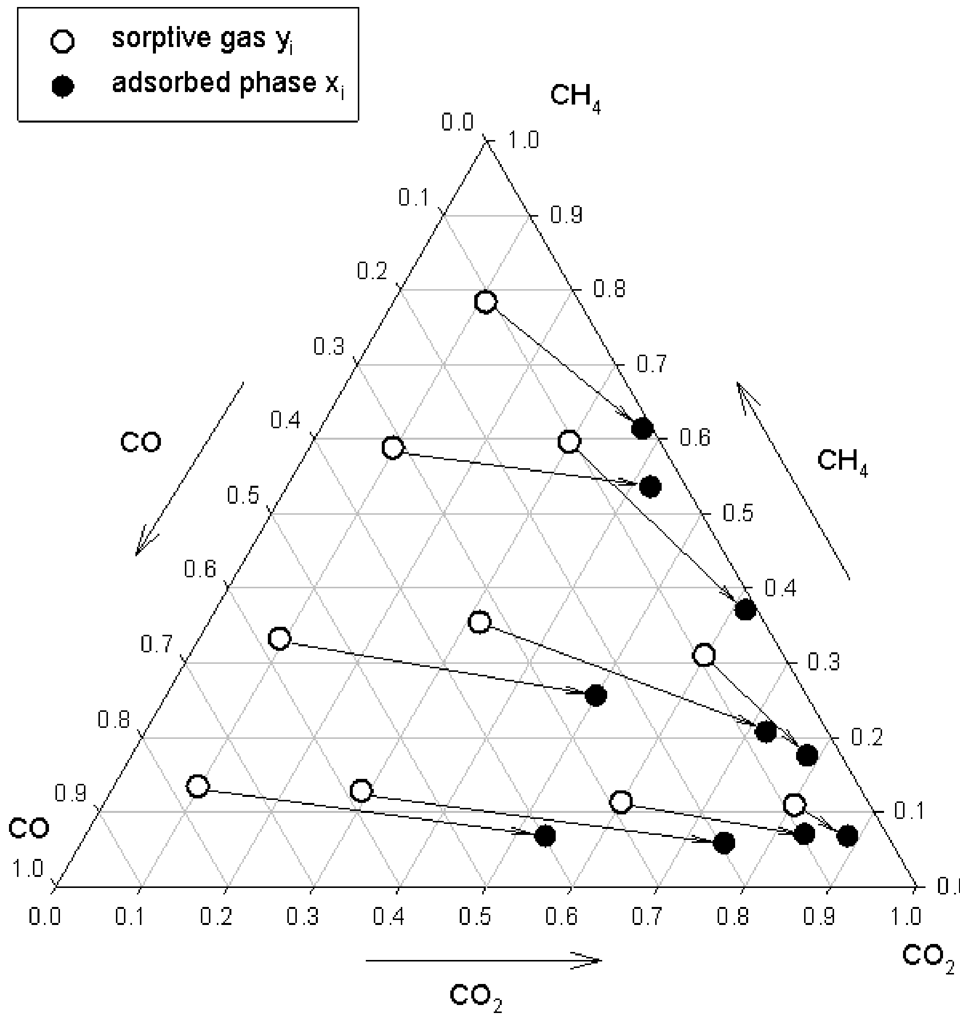

Adsorption equilibria of ternary gas mixture $CO_2/CH_4/CO$ (molar concentrations of the sorptive gases y (○), molar concentrations of the adsorbed phases x (●)) at 293K and 0.2MPa on ACAL.

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$CO_2/CH_4/CO$ T=293K ACAL		f_m , σ %				
		x_{CO2} (adsorbed phase)	x_{CH4} (adsorbed phase)	n_{CO2} (partial load)	n_{CH4} (partial load)	$n_{tot}= n_{CO2} + n_{CH4} + n_{CO}$
0.2 MPa	2LAI	f_m=156 σ =200	**23.8** **30.0**	**4.65** **6.58**	80.1 118	16.1 17.9
	IAST	**161** **199**	35.0 39.8	10.3 12.7	**46.8** **71.4**	**2.73** **3.47**
1.0 MPa	2LAI	**14.2** **18.0**	574 1250	**9.03** **11.1**	705 1540	15.4 20.0
	IAST	**16.5** **18.6**	**424** **924**	17.4 19.2	**510** **1120**	**11.0** **13.8**

- Relative mean deviation (f_m)

$$f_m = \frac{1}{N} \sum_{i=1}^{N} \left(\frac{|n_{PRE} - n_{EXP}|}{n_{EXP}} \right)_i$$

- Relative dispersion (σ)

$$\sigma^2 = \frac{1}{N} \sum_{i=1}^{N} \left(\frac{n_{PRE} - n_{EXP}}{n_{EXP}^2} \right)_i^2$$

Statistical uncertainties (f_m, σ) of coadsorption data $CO_2/CH_4/CO$ on ACAL at 293K and 0.2MPa, 1.0MPa predicted from pure adsorption data by two isotherms.

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Summary and Conclusion

- **Measurement of Adsorption Equilibria of Pure Gases CO, CO_2 and CH_4 on industrial activated carbon (ACAL) at T=293K, p=0 … 1.1MPa.**
- **Data Correlation and Prediction of Binary and Ternary Mixture Adsorption: 2LAI, IAST.**
- **Measurement of Coadsorption Equilibria of Binary Gas Mixtures (CO_2/CO, CO_2/CH_4, CO/CH_4) and Ternary Gas Mixture (CO_2/CH_4/CO) at T=293K, p=0.2MPa ; 1.4MPa.**
- **Prediction vs. Experiment:**

  n_{tot}, n_{CO2} : good approximation (f_m= 3 – 20%).

  n_{CH4} and n_{CO} : can not be predicated (f_m>100% (IAST))!

  Increasing pressure leads to increasing f_m and σ.

Development of more effective thermodynamic models for mixture adsorption and/or providing of more accurate experimental data for coadsorption isotherms is necessary!