

# BINARY GAS ADSORPTION EQUILIBRIA FROM GRAVIMETRIC ADSORPTION DATA

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## Introduction

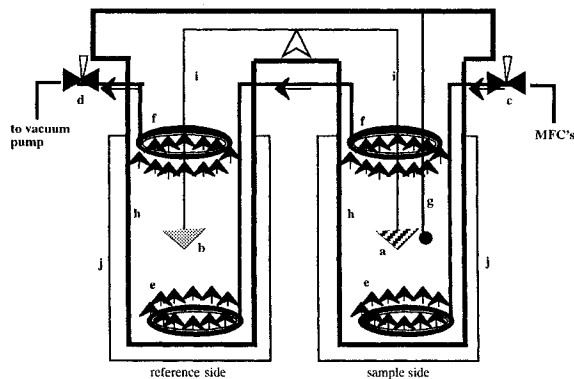
For the development and design of adsorptive gas separation processes accurate equilibrium adsorption data are essential.

The main problem in gravimetric mixed gas adsorption studies is the unknown composition of the adsorbed phase. In this work the rigorous thermodynamic method of Van Ness [1] is used to calculate the adsorbed phase composition from the total adsorbed weight of a methane-carbon dioxide mixture on activated carbon. This is a purely thermodynamic analysis, involving no other assumptions than those present in the Gibbs adsorption theory [2]. The results show deviations from Raoult's law in the adsorbed phase. The activity coefficients are correlated by the Wilson equation.

Furthermore, the experimental data are correlated with the Extended Langmuir (EL) equation, the Ideal Adsorbed Solution (IAS) theory and the Real Adsorbed Solution (RAS) theory.

## Experimental

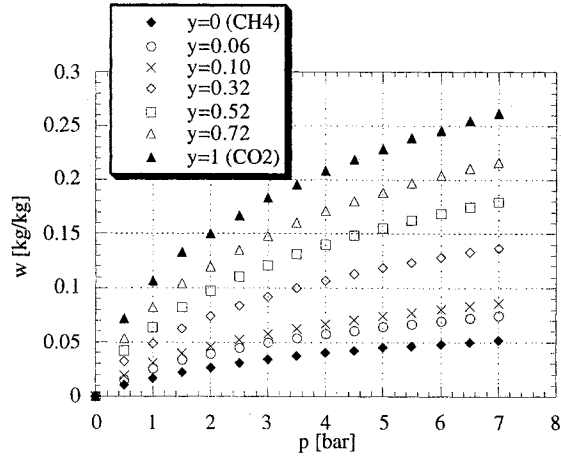
Gravimetric adsorption measurements were performed using a fully automated Intelligent Gravimetric Analyser (IGA, Figure 1) of Hiden Analytical (UK). Norit RB 1 activated carbon adsorbent and high purity (>99.996 V%) methane and carbon dioxide were used.



**Figure 1.** Gravimetric mixed gas adsorption apparatus; (a) sample, (b) reference weight, (c,d) computer controlled needle valves, (e,f) diffuser/collector rings, (g) thermocouple, (h) stainless steel tubes, (i) gold chain hang-down, (j) water-jacket.

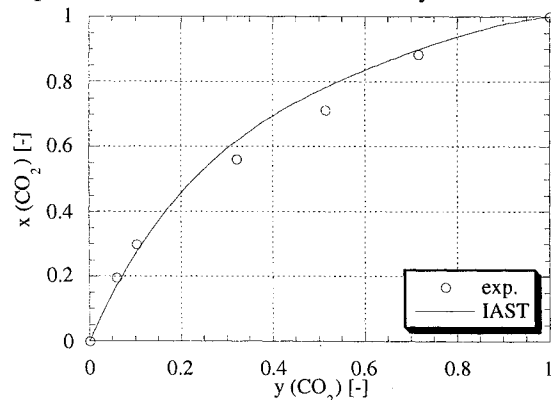
## Results and Discussion

The gravimetric single and mixed gas isotherms are shown in Figure 2.

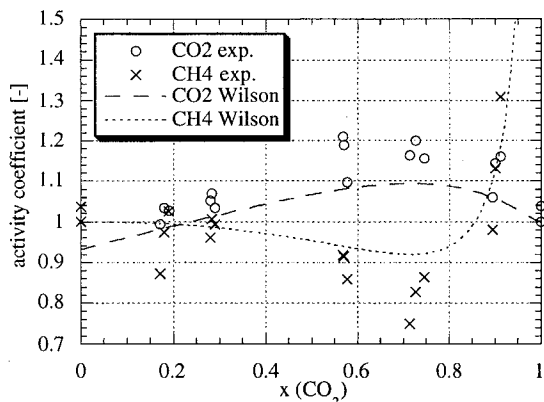


**Figure 2.** Equilibrium adsorbed weight ( $w$ ) of carbon dioxide-methane mixtures for several gas phase compositions ( $y$ ) at 302.9 K.

Using the method of Van Ness the adsorbed phase composition was calculated. The results are given in Figure 3 for 1 bar together with the adsorbed phase composition calculated by the IAS theory which is based on Raoult's law. The activity coefficients shown in Figure 4 were calculated from the difference between the experimental results and the IAS theory.



**Figure 3.** Adsorbed phase composition ( $x$ ) as a function of gas phase composition ( $y$ ) for carbon dioxide-methane mixed gas adsorption at 302.9 K and 1 bar.

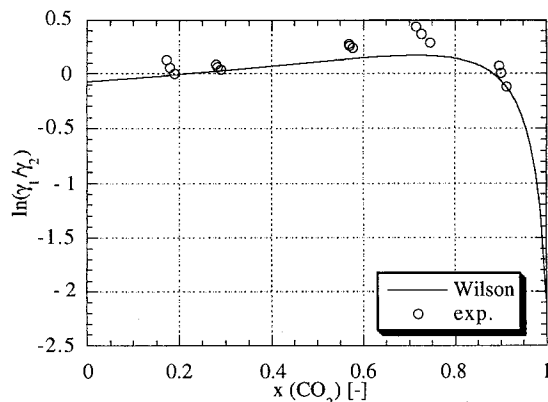


**Figure 4.** Experimental activity coefficients and a simultaneous fit of the Wilson equations for carbon dioxide and methane at 302.9 K and a constant reduced spreading pressure of 5.1 mol kg<sup>-1</sup>.

The activity coefficients ( $\gamma_i$ ) of both components as a function of the adsorbed phase composition must satisfy the Gibbs-Duhem equation, which provides a thermodynamic consistency test:

$$\int_0^1 \ln \left( \frac{\gamma_1}{\gamma_2} \right) dx_1 = 0 \quad (T, \pi = \text{constant}) \quad (1)$$

Figure 5 shows good agreement between the experimental data and Equation 1.



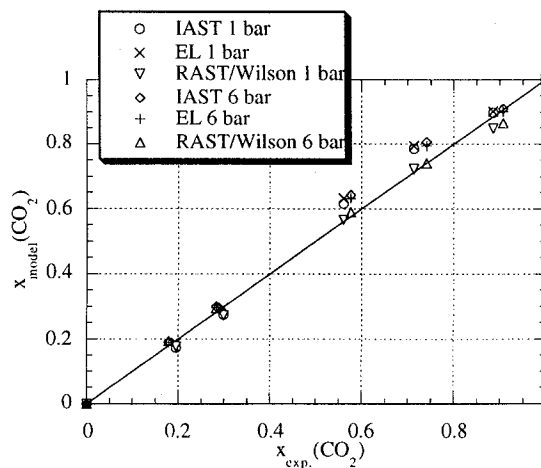
**Figure 5.** Thermodynamic consistency test of the experimental activity coefficients presented in Figure 4; 1=CO<sub>2</sub> and 2=CH<sub>4</sub>.

The variation of the activity coefficients with the adsorbed phase composition presented in Figure 4 deviates from the behaviour we would expect. The interaction parameters in the Wilson equation, shown in Table 1, suggest a large effect of carbon dioxide on methane ( $\Lambda_{12}$ ) and a minor influence of methane on carbon dioxide ( $\Lambda_{21}$ ) which can not be explained by CO<sub>2</sub>/CH<sub>4</sub> interactions alone. Probably the adsorbent surface significantly contributes to the adsorbed phase behaviour, as was shown by Myers [3] for a simple heterogeneous 2-site model.

**Table 1.** Interaction parameters in the Wilson equation (1=CO<sub>2</sub>, 2=CH<sub>4</sub>).

$\Lambda_{12}$	2.9
$\Lambda_{21}$	0.018

In Figure 6 the adsorbed phase composition calculated by the Extended Langmuir equation, the IAS Theory and the RAS Theory using the Wilson equation are shown. The EL and IAS Theory perform equally well.



**Figure 6.** Comparison of mixed gas adsorption models for the calculation of carbon dioxide-methane mixed gas adsorption on activated carbon at 302.9 K.

## Conclusions

The Real Adsorbed Solution Theory with the Wilson Equation to account for non-ideality gives better fit with the experimental mixed gas adsorption data than the Extended Langmuir Equation and the Ideal Adsorbed Solution Theory.

An alternative theory to calculate activity coefficients is required to account for the contribution of the adsorbent surface to the behaviour of the adsorbed mixture.

## Acknowledgements

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## References

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2. Ritter, J.A. & Yang, R.T. *Ind. Eng. Chem. Res.*, 1989, 28, 599-608.
3. Myers, A.L. *AIChE J.*, 1983, 29, 691-693.