

# THERMODYNAMICS AND KINETICS OF WATER UPTAKE AND RELEASE BY CARBON ADSORBENTS

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## Introduction

Recent work by the author revealed remarkably high heats of adsorption of water vapour on active carbons which contrast strongly with the conventionally determined adsorption isotherms [1]. The latter indicate very low water uptakes at low water partial pressures. The flow microcalorimetric work of the author has now been extended to a number of different carbons and graphites and the rates of heat evolution as well as the kinetics of water uptake determined at room temperature. This abstract summarises some of this work and discusses the significance of the results.

## Experimental

The rates of water adsorption / desorption and the accompanying rates of heat evolution / absorption have been determined in a new model of Microscal Flow Microcalorimeter (FMC), an FMC-4110, which was recently described [2].

Adsorption experiments were carried out on 5 – 7 mg samples of the carbons mixed with quartz sand to fill the volume of the adsorption cell in the FMC (170  $\mu$ l). Prior to saturation with water vapour, dry helium was passed through the samples at 25°C for 20 hours at a flow rate of 1 ml min<sup>-1</sup>. Adsorption took place from He containing 0.95  $\mu$ mol of water per cm<sup>3</sup> of the gas. The gas passed through the carbon bed at a constant rate of 1 ml min<sup>-1</sup>.

## Results and Discussion

Figure 1 shows the rate of heat evolution and the corresponding rates of water uptake measured by the FMC. As can be seen, the kinetics are high initially and become slow towards the end of the process. The total uptake of water is 22 mmol g<sup>-1</sup>.

The molar heats of adsorption shown in Figure 2 give valuable information on the nature of adsorption processes on graphitic active carbons and graphite powder (very similar results are obtained for synthetic graphite powders).

The heats are high at small uptakes and then decrease to 44 kJ mol<sup>-1</sup> as the adsorption increases before rising again for

certain types of active carbons [1]. The latter phenomenon is a post adsorption process, believed to be due to structural changes in the adsorbent. It should be noted that the measurements of isosteric heats of water adsorption on similar active carbons reported in the literature do not reveal the occurrence of the remarkably high initial heats obtained in this work [3].

The high heats of water adsorption are not confined to microporous graphitic materials such as active carbons. Synthetic and natural graphite powders, which are not microporous, do strongly adsorb water as shown in Figure 3. In this case the total uptake of water vapour at 25°C is 0.033 mmol g<sup>-1</sup>. The heats of adsorption start at about 100 kJ mol<sup>-1</sup>, and show a small secondary increase for a water coverage between 30–40% before dropping to the heat of water condensation closer to 100% coverage.

Graphite powders with very low proportions of polar sites, such as SP1 materials, do not give any measurable adsorption of water. It seems, therefore, that the adsorption of water is entirely dependant on the presence of polar sites on the carbon surfaces.

## Conclusions

Adsorption of water vapour on microporous graphitic adsorbents represented by an active carbon and a synthetic graphite powder gives surprisingly high molar heats of adsorption at low surface coverages. These phenomena indicate the important effect that the adsorbed water may have in selective adsorption and catalytic properties of the carbons in the presence of water and, in the case of graphite powders, on their lubricating and frictional properties.

## References

- [1] Groszek AJ, Aharoni C. Study of the Active Carbon-Water Interaction by Flow Adsorption Microcalorimetry. *Langmuir* 1999; Accepted for publication.
- [2] Groszek AJ. Flow Adsorption Microcalorimetry. *Thermochemica Acta*; 1998; 312; 133–143
- [3] Sircar S, Golden TC, Rao MB. Activated carbon for gas separation and storage. *Carbon* 1996; 34(1); 1–12

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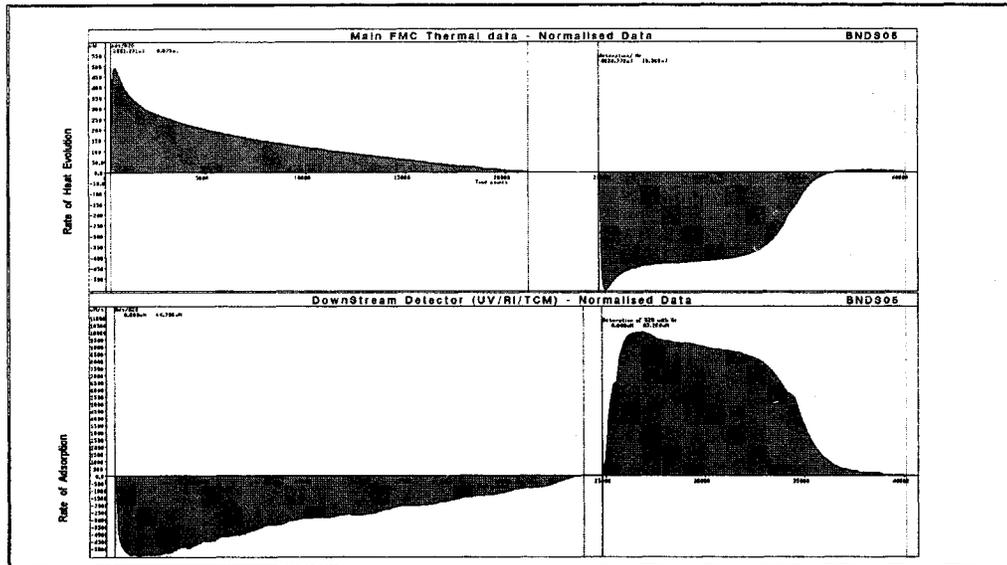


Figure 1 – Adsorption of water from He on 6.5 mg of active carbon CAL

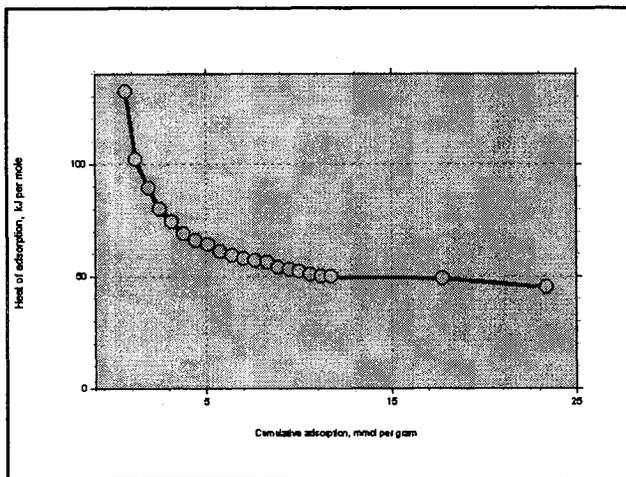


Figure 2 – Molar heats of adsorption of water on carbon CAL at 25°C – Changes with surface coverage

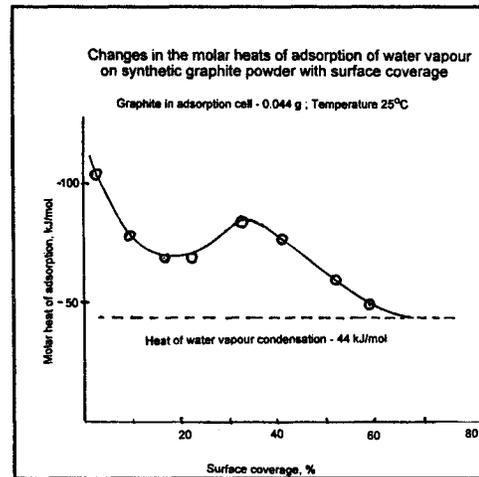


Figure 3 – Molar heats of adsorption of water on synthetic graphite at 25°C – Changes with surface coverage