

# MORPHOLOGY OF CARBONS DEDUCED FROM PHYSISORPTION ISOTHERMS: II. ACTIVATED CARBONS

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## Introduction

The nature of the pores in activated carbons is important in the many aspects of their uses in separation, sorption, purification, etc. Elucidation of the porosity is important and "The most common methods for determination are -- nitrogen or argon adsorption methods"(1) Previous reports(2) have shown that the Autosheilding Potential (ASP) generally defines the thermodynamics of the physical adsorption processes for surfaces and pores "in the micropore domain (where) the Kelvin equation is not valid"(1). The sorption potential,  $E$  is related to the relative pressure:

$$E = -RT \ln[P/P(0)] \quad \text{Equation 1}$$

and for domains of physical adsorption there should exist a relationship for the amount of sorption,  $\Gamma$ :

$$E/E(\text{zero}) = \exp -[\Gamma] \quad \text{Equation 2}$$

for monolayer and multilayer adsorption on an open surface.

## Experimental

Fisher Activated Coconut Shell Charcoal (ACSC, 6-14 mesh, Lot Number 5-685-A) is known to have considerable merit for sorption applications in many fields (4). The nitrogen (99.999%) sorption isotherm at 77.2 K was acquired with a Quantasorb volumetric instrument for relative pressures ranging from  $9.5 \times 10^{-6}$  to 0.991, after 300 C outgassing in situ overnight. A small amount of hysteresis was noted on desorption as noted in isotherm of Figure 1.

## Results and Discussion

The small amount of external surface, available for unhindered monolayer-multilayer formation, significant only above ca. 0.90  $P(0)$ . The line represents the adsorption process per se as defined by the ASP analyses (Figure 2) which occurs as shown by the solid line and serves well to describe the nebulous statistical adsorbed layer "thickness,  $t$ " used in comparison plots and most pore size distribution calculations.

Indeed, the ASP plot bears an uncanny resemblance to the comparison ( $\alpha$ ,  $n$ ,  $t$ ,  $\theta$ , etc.) plots(5) where 2 or more linear regimes are noted. In addition the low pressure data are analyzed and show consistency

below 0.0005  $P(0)$ ,  $0.5 \times \Gamma[0.40P(0)]$ , the lowest point offered in most reference isotherms. This is a direct method and avoids errors associated with interpolation to the pressures dictated by the tabular "standard isotherm," even if it is a true representation of the chemistry and crystal structure of the surface of the substrate in question.

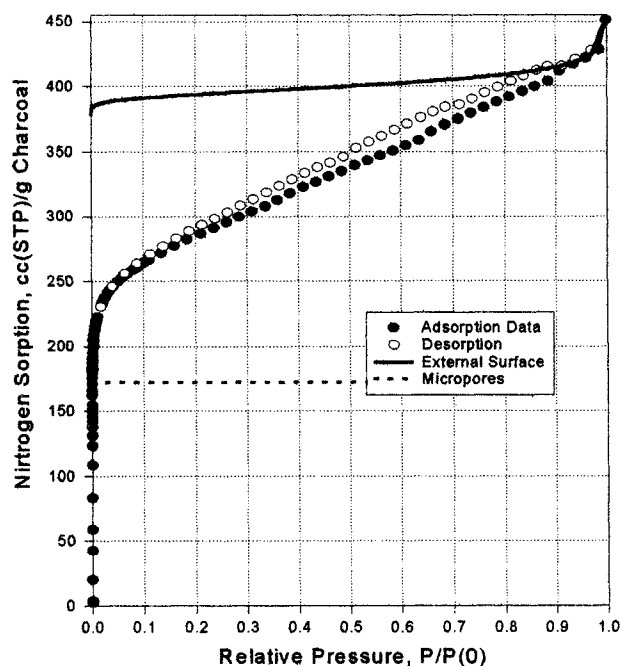
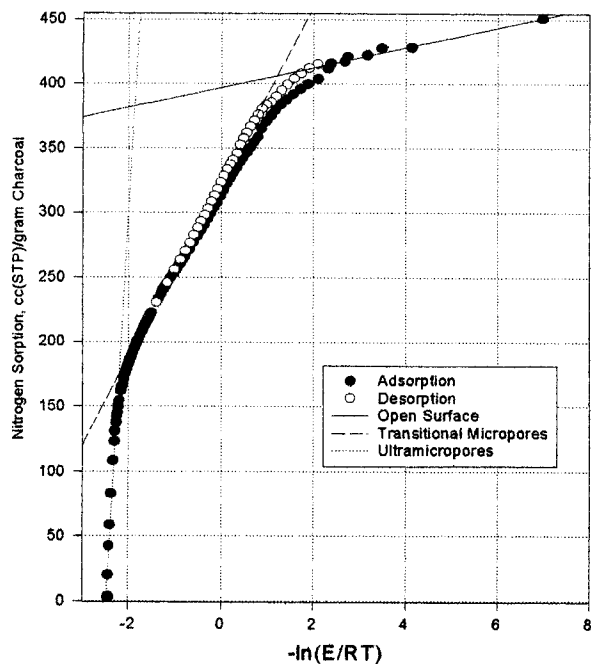


Figure 1. Nitrogen Sorption: Activated Coconut Shell Charcoal 77,2 K.

Even more important is the direct evaluation of the energetics associated with each regime. The ASP mechanism(3) is in play for each of these sorption domains since the basic assumptions are valid for the different energy ranges and the saturation capacity for each of these is a limiting volume capacity, rather than the area capacity, in Equation 2 is applicable. The regression parameters for the three regimes and the quality of fit are given in Table 1 based on direct analyses of the experimental data in cc(STP)g(char).

Table 1. ASP Parameters: Nitrogen on ASCS

Segment	Intercept	Slope	r squared
First	1574.5	635.0	0.9494
Second	323.8	67.75	0.9994
Third	397.4	7.762	0.9687
	cc(STP)/g	cc(STP)/g	

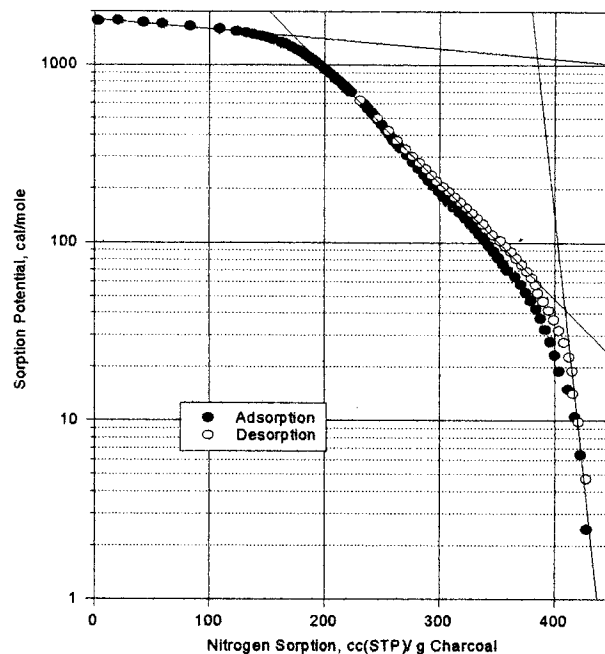


**Figure 2. ASP Plot Nitrogen on ACSC. All of the data are described as three distinct linear segments.**

The sorption potential energy variations are emphasized with a change of coordinates and energy units as given in Figure 3. This is a more traditional thermochemical presentation and equally relates the domains for the specific sorption processes. Evaluation of pore sizes and distributions still involves modeling geometry with respect to the thermochemical observations [a “*contradictio adjecto*” according to Horvath (1)]. The ASP analyses provide a functionality for relevant adsorption potential distributions(6).

### Conclusions

- Inert gas physisorption on activated chars is well described in terms of an autoshielding potential over a wide range of sorption (relative pressure).
- The errors associated with the “standard curve” are circumvented.
- The high pressure regime is used to evaluate the surface area, based upon the unrestricted formation of monolayer and multilayers on surface of the given char under study. This equivalent to “using data in the  $\alpha_s$  range from 1.5 to 2.5.”(6)
- The ASP plots are equivalent to comparison plots and provide direct energy terms associated with the various internal regimes of the char.
- ASP plots have the added benefit of allowing analyses at much lower pressures (sorption).
- Evaluation of pore sizes and distributions from these thermochemical relations can be frustrating but well worth the effort.



**Figure 3. Sorption Potential: Nitrogen on ASCS.**

- Modeling of gas condensation in micropores must be consistent with the thermochemistry defined by the ASP results..
- Additional studies on other carbon molecular sieves and other microporous materials are warranted.

### References

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7. The contributions and discussions with T.D. Burchell and M.R. Rogers of the Carbon Technology Group of The Oak Ridge National Laboratory are greatly appreciated.