Gas Sorption Analysis for Advanced Nanopore Structure Characterization

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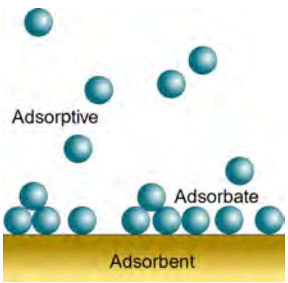
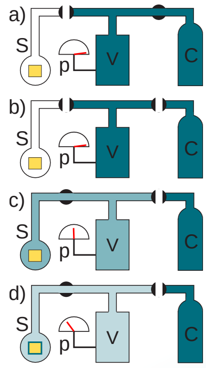
Physisorption Basics



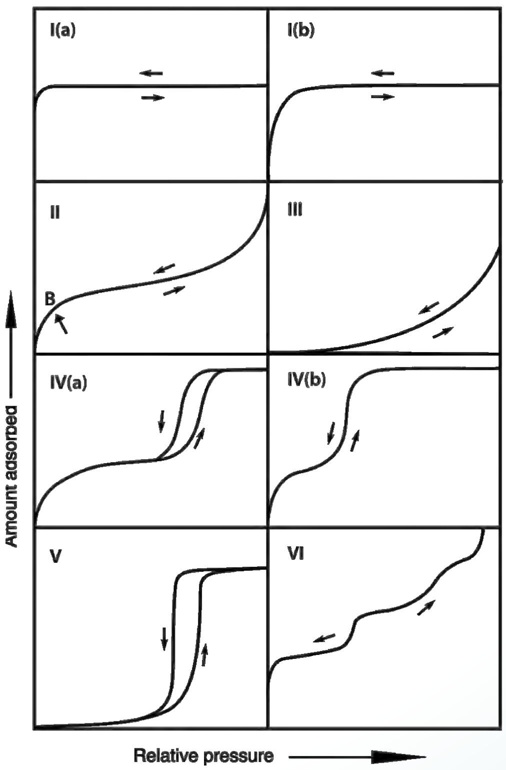
London dispersion forces lead to an attractive interaction between gas molecules and solid surfaces. The resulting change in potential energy of the particles induces a change of the equilibrium phase close to the surface. This causes the formation of an adsorbed layer.
If the behaviour of the gas is well known, it is possible to get information on the solid surface.

Measurement Principle



a. Gas is filled from a storage cylinder (C) into a reference volume (V).
b. The valve between C and V is closed, the pressure (p) is recorded.
c. The valve to the sample environment (S) is opened. The larger volume leads to a drop of p.
d. The formation adsorbate takes particles from the adsorptive, which leads to an additional drop of p. This additional drop of p is proportional to the adsorbed mass.

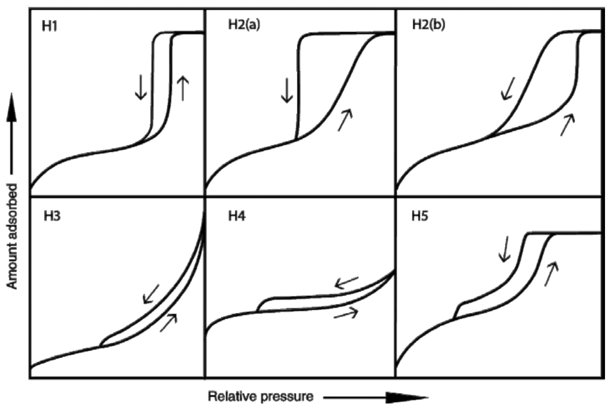
Classification of Isotherms



The shape of the sorption isotherm depends on the physical state of the gas, the adsorbed material and the amount of adsorbed material. It can be used to classify the isotherm and thereby to identify the underlying process. The isotherm types according to IUPAC are:

I(a): Ultra-microporous system with pores smaller than ~1 nm. The limit in uptake is controlled by micropore volume.
I(b): Microporous system with some small mesopores (up to ~2.5 nm).
II: Sorption of gases on non-porous or macroporous surfaces. The knee labelled "B" indicates monolayer formation. A more gradual slope is caused by simultaneous onset of multilayer formation. No saturation plateau is reached.
III: Weak interactions between adsorbent and adsorbate. The molecules form clusters at favourable sites, but no film is formed. No identifiable monolayer formation at low relative pressures (i.e., no point B).
IV(a): Mesoporous system. The initial shape is identical to Type II, but at higher pressures pore condensation occurs. Condensation occurs at higher pressures for larger pores. The final amount of adsorbed material is finite. The width of the hysteresis loop depends on the adsorption system and temperature. It is observed for mesopores exceeding a critical size.
IV(b): Similar to Type IV(a) but without hysteresis loop as observed in smaller pores.
V: Similar to Type III at low pressures but mesoporous behaviour. At higher pressures, the pores are filled.
VI: Layer-by-layer adsorption on non-porous, highly uniform surface. The height of the steps depends on the capacity of a monolayer.

Classification of Hysteresis Loops



H1: Narrow range of uniform mesopores. The desorption branch corresponds to a reversible liquid-vapour transition. The position of the adsorption branch is determined by the metastability of the adsorbed layer.
H2(a): Pore blocking by necks with narrow distribution. Cavitation induced evaporation during desorption, once the blocked necks have opened.
H2(b): Similar to H2(a) but with a wider size distributions of necks.
H3: Adsorption branch is similar to Type II isotherm. Typical for non-rigid aggregates of plate-like particles as well as for a network of not completely filled macropores.
H4: Adsorption branch is similar to composite if isotherm Types I and II. Found for aggregated microporous crystals.
H5: Material containing both open and partially blocked mesopores.

The corresponding graphs are taken from M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol , K.S.W. Sing (2015) "Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)", *Pure Appl. Chem.*, **87(9-10)**, 1051-1069

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