

23f Hysteresis in Sorption by Mesopores

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Hysteresis is displayed in systems in which two different reactions with two degrees of freedom involving the same reactants can take place at various ranges of pressure, if there is an intermediate range at which both reactions are thermodynamically feasible, but are mutually exclusive and cannot take place simultaneously.

If the pressure is raised from a low value at which the reaction favored at low pressure is the only one that can take place to the intermediate range at which both reactions are feasible, the reaction that was taking place at low pressure is the only reaction that takes place at the intermediate range and an irreversible switch to the reaction favored at high pressure takes place at the high pressure end of the intermediate range. If the pressure is started at a high value and is subsequently lowered, the reaction favored at high pressure is the only one that takes place at the intermediate range and the switch to the other reaction takes place at the low pressure end of the intermediate range. Thus the switches from one of the reaction to the other takes place at two different values of the pressure, and look like the opposite directions of the same reaction

In sorption by a mesopore, the pore filled by capillary condensation contains a layer of adsorbate at the proximity of the pore walls with properties different from those of the “condensate” at the core, its density varies with the pressure and it obeys an adsorption isotherm. However the adsorption energy for an adsorption process in which the adsorbate is in contact with condensate differs from the adsorption energy for a process in which the adsorbate is in direct contact with the vapor phase, since the replacement of the interface adsorbate - vapor by an interface adsorbate - condensate causes a change of the effective energy of adsorption; it is increased by an amount that can be estimated from the surface area of the adsorbate and the surface energy per unit area at the liquid - vapor interface

Thus the above mentioned conditions for the occurrence of hysteresis apply to this system. Two adsorption processes with different adsorption energies can take place: “adsorption with adsorbate in contact with vapor” and “adsorption with adsorbate in contact with condensate”; the former is favored at low pressure, and the later at high pressure. There is an intermediate range of pressure at which both processes are thermodynamically feasible but they are mutually exclusive, since the pore can be either empty of condensate or filled with condensate