

Thermodynamic and kinetic sorption
at accumulation of gases in nanomaterials
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Thermodynamic sorption typically occurs being favored by enthalpy of bonding sorbate molecules to a surface (or matrix) of a sorbent. In the present report some types of kinetic sorption are considered.

If the molecule (or atom) is placed in a strongly constrained space (pore or nanotube), with a characteristic transversal dimension (d), much less than a mean free path length of the free motion l in a macrovolume of a gas (with concentration of molecules n_o and pressure P_o), then it in general collides with the walls of a pore, but not with the adjacent molecules up to the moment, when in the model of ideally smooth walls and ideal gas $\sigma \cdot n_{loc} \cdot d \leq 1$, (where σ - is the cross-section of encounters of molecules with each other and n_{loc} - concentration of molecules in the considered confined space). If $n=P/kT$ (for ideal gas), then in nanopores the pressures may be created up to $P_{loc} \leq kT/\sigma d$, that by far outweigh the mean pressure P_o in the macrovolume, and the coefficient of accumulation of a gas in an individual nanopore will be $\xi_{loc}=n_{loc}/n_o \leq l/d$. At this the initial rate of accumulation of molecules of the gas sorbed by the individual «open» nanopore at $d>>(\sigma)^{1/2}$ will be $W_{loc} \approx n_o \pi d^2 V/24$ (where V - is the mean velocity of molecules at this temperature). At $d \sim 1-10$ nm the value of ξ_{loc} may be equal to 10^2-10^3 . The mean coefficient of accumulation in a macrovolume will be $\xi_{av}=\xi_{loc}\beta$ (where β - the percentage of the volume of the sample, occupied by the nanopores considered). For example, for the molecules of oxygen, atoms of argon and others in nanopores of polymeric and mineral sorbents the experimentally achieved coefficient of accumulation was equal to two orders of magnitude.

For keeping gas accumulated, it is used a thermodiffusion «lock» with polychronous kinetics of micropermeability. So, for the polystyrene composites the spectrum of activation energies E of micro and nanodiffusion O_2 fall in the interval from 5 to 20 kcal/mol, while enthalpy of sorption is equal to $\Delta H = -1.8$ kcal/mol. An analogous effects are typical also for the carbon nanomaterials. At this the accumulation of molecular hydrogen in nanotubes, because of the effective injection of electrons, may be accompanied by the transformation of it in a «quasi-metallic» state, what increases abruptly the density of a sorbat, and, correspondingly increases the effects of accumulation (especially at corresponding doping of nanotubes).

Experimental differences of the effects of thermodynamic and kinetic sorption are consist in the temperature dependence of the kinetic of sorption-desorption processes. The process of the thermodynamic sorption is an equilibrium one with respect to the enthalpy of desorption ΔH with the opportunity of the possible existence of a spectrum of values of ΔH (especially in the case of mineral sorbents). For the kinetic sorption the process of desorption is nonequilibrium and it is determined by the kinetic of the departure of the

molecules of a sorbent from nanopores through the thermodiffusion «lock» (with the corresponding energy of activation of diffusion E). In the case of ideally «smooth» and «open» nanopores the desorption of the ideal gas will be characterized by the kinetic without the activation. Finally, at including of the active centers with the essential entropy of sorption ΔH it will be observed the superposition of the diffusion and sorption-desorption processes¹.

Therefore, the predominance of the kinetic and/or thermodynamic effects of sorption it is possible to separate investigating the kinetic of sorption-desorption processes at different temperatures. The effect itself of the kinetic sorption and thermodynamic «lock» it is possible to use at accumulation of gas molecules in nanomaterials, including hydrogen molecules in nanotubes and other sorbents.

Reference

1. A.I.Mikhailov, S.I.Kuzina «Kinetic Inhomogeneity of Diffusion and Solubility of Gases in Polymers at Low Temperatures», *Eur. Polym. J.*, 26, 105-116 (1990).