

Electronic Supplementary Information
for
Monte Carlo study of chemical reactions equilibria
in pores of activated carbons

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Table S1

Criteria of acceptance for different trial moves (N_i – the number of i -th kind of molecules, T – temperature, k_B – Boltzmann constant, V – volume of the simulation box, ΔU – the change in configurational energy, Γ – reaction quotient, Z_i – the activity of i -th component ($Z_i = p_i/k_B T$ and p_i is the pressure of i -th component in the bulk phase); we have assumed the ideality of the gases).

displacement of random molecule	reaction steps (dimerization)
$P_{acc} = \min \left\{ 1; \exp \left[-\frac{\Delta U}{k_B T} \right] \right\}$	- forward ($A + A \rightarrow B$)
creation of molecule of i -th kind	$P_{acc} = \min \left\{ 1; \frac{\Gamma (N_A - 1) N_A}{V N_B + 1} \exp \left[-\frac{\Delta U}{k_B T} \right] \right\}$
$P_{acc} = \min \left\{ 1; \frac{Z_i V}{N_i + 1} \exp \left[-\frac{\Delta U}{k_B T} \right] \right\}$	- backward ($B \rightarrow A + A$)
annihilation of molecule of i -th kind	$P_{acc} = \min \left\{ 1; \frac{V N_B}{\Gamma (N_A + 1)(N_A + 2)} \exp \left[-\frac{\Delta U}{k_B T} \right] \right\}$
$P_{acc} = \min \left\{ 1; \frac{N_i}{Z_i V} \exp \left[-\frac{\Delta U}{k_B T} \right] \right\}$	
reaction steps (isomerization)	reaction steps (synthesis)
- forward ($A \rightarrow B$)	- forward ($A + B \rightarrow C$)
$P_{acc} = \min \left\{ 1; \Gamma \frac{N_A}{N_B + 1} \exp \left[-\frac{\Delta U}{k_B T} \right] \right\}$	$P_{acc} = \min \left\{ 1; \frac{\Gamma N_A N_B}{V N_C + 1} \exp \left[-\frac{\Delta U}{k_B T} \right] \right\}$
- backward ($B \rightarrow A$)	- backward ($C \rightarrow A + B$)
$P_{acc} = \min \left\{ 1; \frac{1}{\Gamma} \frac{N_B}{N_A + 1} \exp \left[-\frac{\Delta U}{k_B T} \right] \right\}$	$P_{acc} = \min \left\{ 1; \frac{V N_C}{\Gamma (N_A + 1)(N_B + 1)} \exp \left[-\frac{\Delta U}{k_B T} \right] \right\}$

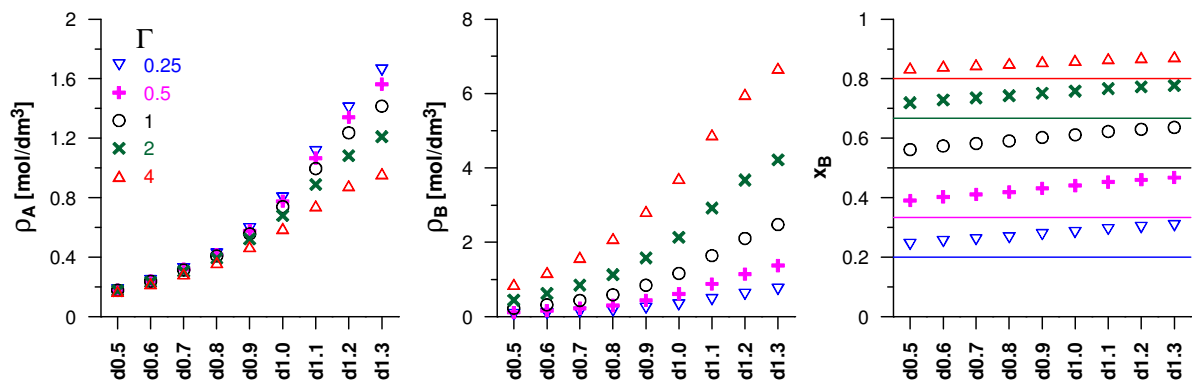


Figure S1. The comparison of the composition of the reacting phase ($T = 298$ K) in pores of all the considered VPCs for the isomerisation reaction ($A \leftrightarrow B$). The data corresponding to different values of the reaction constant (Γ) and the same value of the potential well depth for the product molecules ($\epsilon_{BB}/k_B = 120$ K) have been shown. The subsequent panels present the average densities of the reactant (ρ_A) and the product (ρ_B) in pores (the densities have been calculated per the volume of accessible pores) and the mole fraction of the product in the mixture (x_B). The x_B mole fractions for the reactions in the bulk phase are shown as horizontal solid lines.

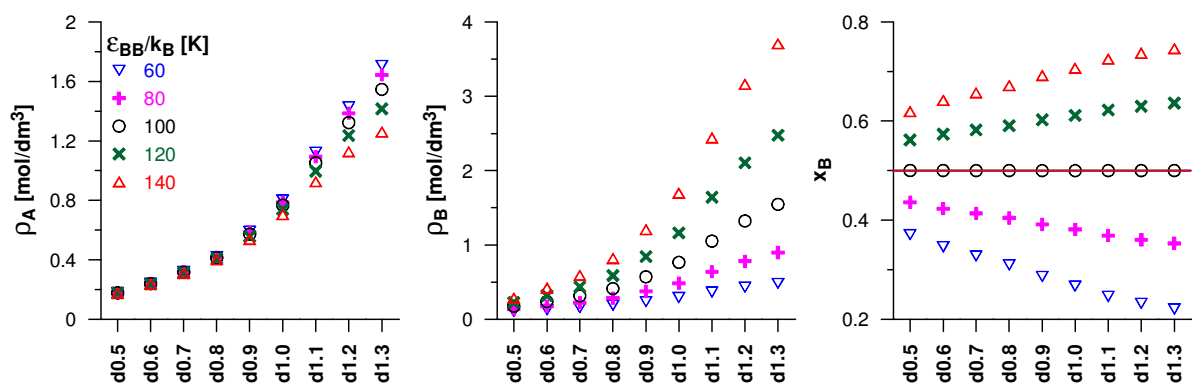


Figure S2. As in Figure S1, but for the fixed value of the equilibrium constant ($\Gamma = 1$) and different values of the potential well depth for product molecules (ϵ_{BB}). The horizontal lines present the x_B mole fraction in the bulk phase (it should be noted that these lines are overlapped).

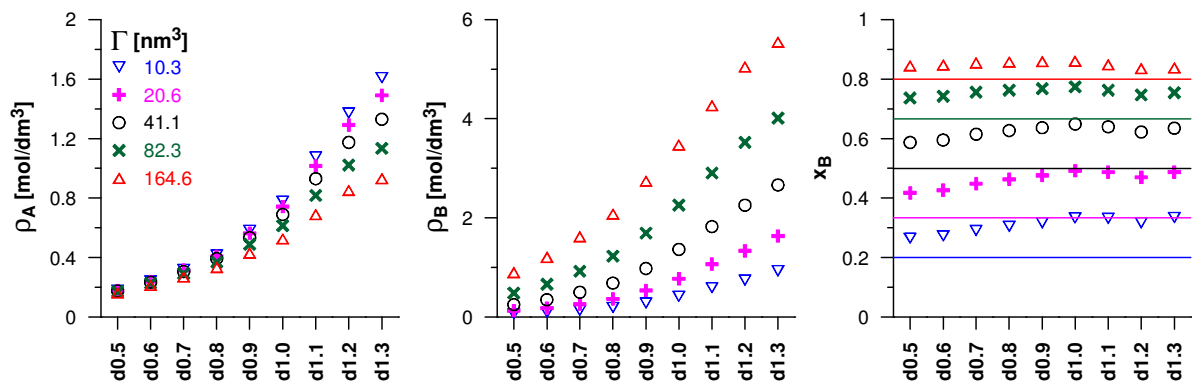


Figure S3. As in Figure S1 but for the dimerisation reaction ($A+A \leftrightarrow B$). The data for different values of the reaction constant (Γ) and the same value of the potential well depth for the product molecules ($\epsilon_{BB}/k_B = 72$ K) have been shown. The x_B mole fractions for the reactions in the bulk phase have been shown as horizontal solid lines.

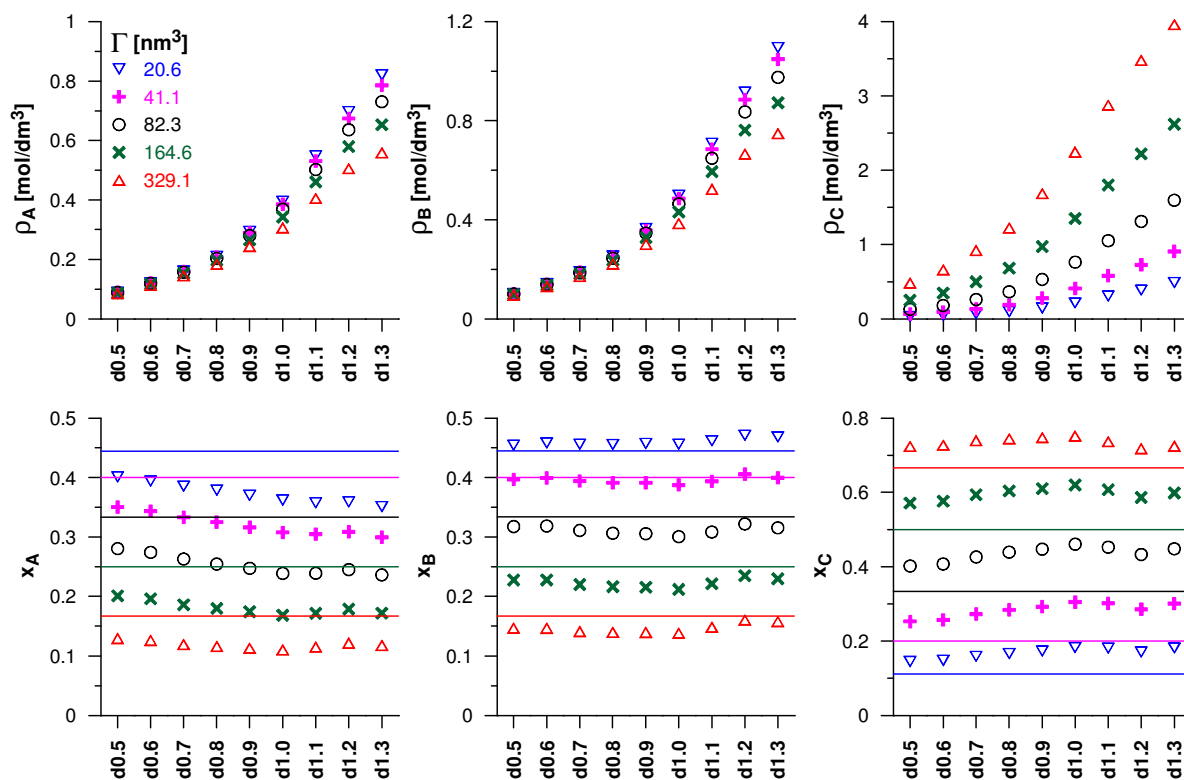


Figure S4. As in Figure S1 but for the synthesis reaction ($A+B \leftrightarrow C$). The data presented correspond to the different values of the reaction constant (Γ) and the fixed values of the potential well depth for the reactant B ($\epsilon_{BB}/k_B = 110$ K) and the product ($\epsilon_{CC}/k_B = 72$ K). The reactants pressure in the bulk phase have been taken as $p_A = p_B = 0.05$ MPa. The upper panels present the average densities of the reacting species (ρ_A , ρ_B and ρ_C). The lower panels show their mole fractions in the mixture (x_A , x_B and x_C). The mole fractions for the reaction taking place in the bulk phase are marked by horizontal lines.

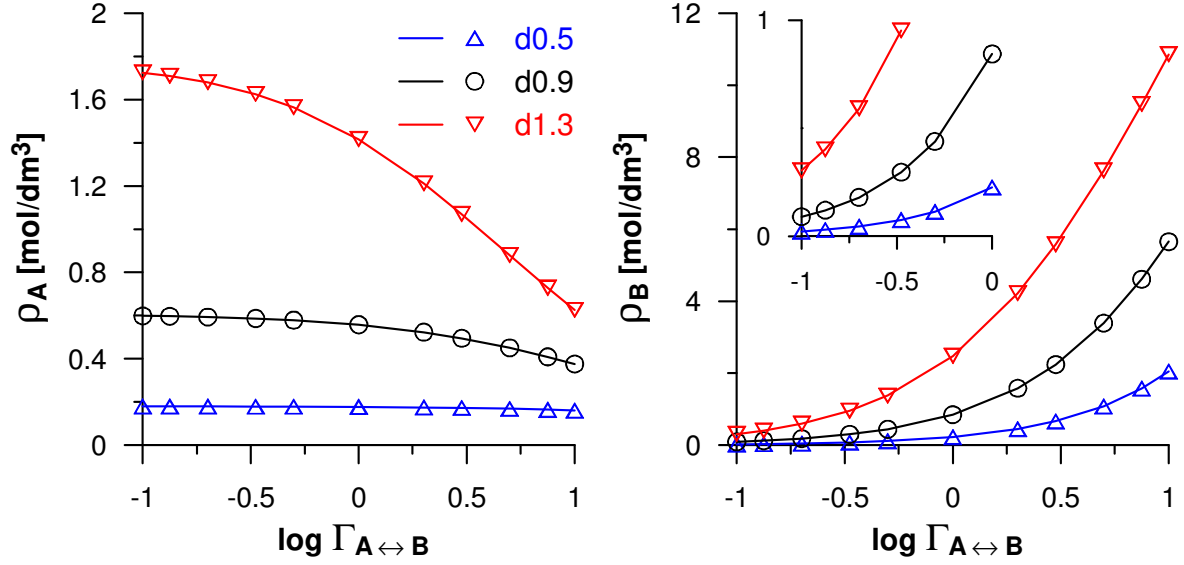


Figure S5. The average densities of the reacting molecules for the isomerisation reaction ($A \leftrightarrow B$) in the selected VPCs as the functions of the equilibrium constant in the logarithmic scale ($\epsilon_{BB}/k_B = 120$ K). Two cases have been considered: (i) the molecules of A have been created and annihilated in the pores according to the GCMC moves (adsorption from gaseous phase), while the B molecules have been formed or destroyed only via the reaction step (the data presented as lines) and (ii) the B molecules could be adsorbed, while the molecules of A have been created or destroyed only during the reaction (the data presented as points). In the case (i) $p_A = 0.1$ MPa for all the systems, and in the case (ii) $p_B = \Gamma_{A \leftrightarrow B} \times p_A$ ($p_A = 0.1$ MPa).

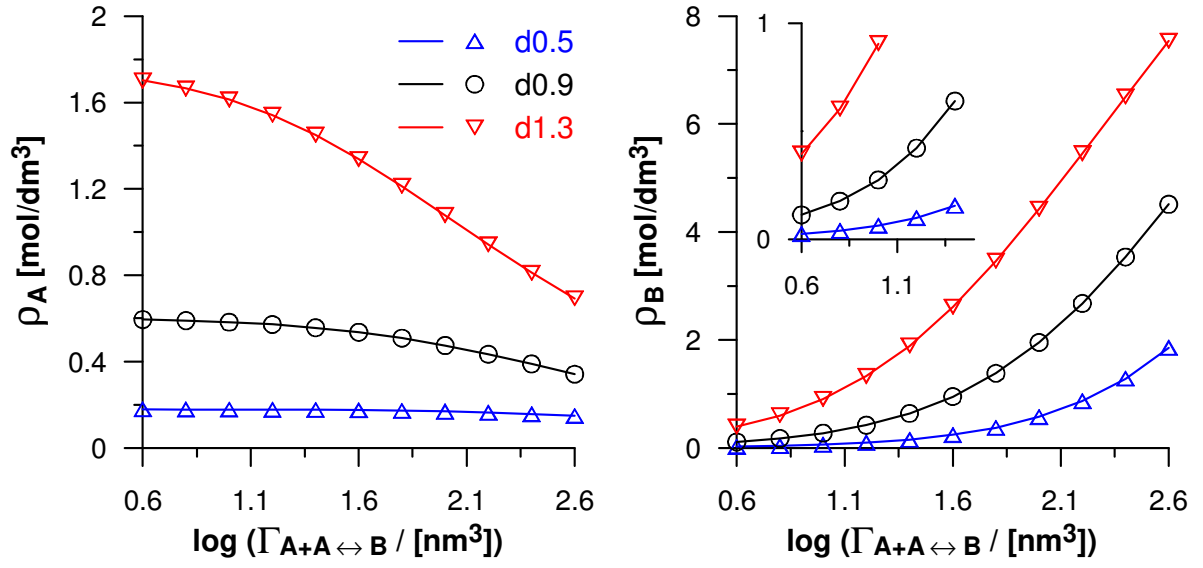


Figure S6. As in Figure S5 but for the dimerisation reaction ($A+A \leftrightarrow B$; $\varepsilon_{BB}/k_B = 72$ K). In the case of the adsorption of B molecules (points), $p_B = \Gamma_{A+A \leftrightarrow B} \times p_A^2 / (k_B \times T)$ and $p_A = 0.1$ MPa.