

SIMULATING CO₂ ADSORPTION AND DIFFUSION ON A GRAPHITE SURFACE

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ABSTRACT

We performed classical molecular dynamics (MD) simulation to understand the mechanism of CO₂ adsorption and transport on graphite surface. The temperature of the system in our simulation was in the range 300-500K. The simulation data show that there are two layers of CO₂ molecules adsorbed on the surface. These two layers have a different behavior. The first CO₂ layer is isolated as it does not exchange molecules with the second layer and is liquid-like, while the second layer exchanges molecules with the gas phase. The layers are separate thermodynamic systems. We use the simple Langmuir model to fit the adsorption isotherm for the second layer. The enthalpy of adsorption is calculated $\Delta H^0 = -16$ kJ/mol. This value is in good agreement with experimental data of adsorption of CO₂ on activated carbon. Along the graphite surface, the diffusion coefficient of CO₂ in the first layer and the second layer are roughly of 10^{-11} m²/s, 10^{-10} m²/s respectively. These values are much smaller than for H₂.

INTRODUCTION

The production of cheap membranes for CO₂ separation is of primary importance for the realization of carbon capture and sequestration technologies.¹ Nano-porous, fibrous, carbonaceous materials are promising candidates from an experimental point of view. In order to make further progress to produce molecular sieve membranes, better knowledge of several issues is needed. Central for good membrane functionality are pore size, surface binding, surface wall transport, pore inlet control, carbon structure and composition.

There are many experimental works and simulations devoted to understand the adsorption of CO₂ on carbon based material such as activated carbon and graphite.²⁻⁵ The adsorption isotherm of CO₂ on active carbon is well described by several models such as Langmuir,² Tóth,⁶ Dubinin-Astakhov (D-A),^{3,7} Reported values for iso-steric enthalpy of adsorption differ a lot and depend on the sorbent used and the condition of adsorption. Saha *et al.* reported that heats of adsorption of CO₂ in Maxsorb II and ACF (A-20) material were around -20 kJ/mol.³ If one uses another untreated activated carbon C3345 material, the heat of adsorption was -14 kJ/mol.² Guo *et al.* reported that the heat of adsorption can vary in the range of (-10 – -28 kJ/mol) depending on the modification condition of the activated carbon material.⁵ Himeno *et al.* also reported an adsorption enthalpy which was in range -16 – -25 kJ/mol) of pure CO₂ on five different commercial activated carbons.⁶

Several theories have motivated the adsorption isotherm of CO₂ on graphite surface and in the slit pores of graphite. Lim *et al.* presented a Langmuir adsorption model and diffusion coefficient ($D_s = 10^{-9} - 10^{-10}$ m²/s) of CO₂ in a narrow pore width ($H = 0.65 - 0.75$ nm) and for temperatures $T = 298 - 318$ K.⁸ While Zhou *et al.* reported these value in wider range of

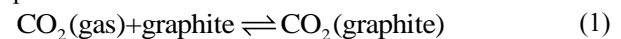
slit pore size ($H = 0.7 - 3.4$ nm) and the values were comparable with Lim *et al.*, Levesque *et al.* calculated the heat of CO₂ adsorption on activated carbon using Monte-Carlo simulations.⁴ The authors discussed the dependence of adsorption enthalpy on the distribution of pore sizes. These works had no distinct CO₂ layers in the pores or on the surface.

This work aims to establish a thermodynamic model for the layers of CO₂ on the graphite surface and find diffusion coefficient for the surface. We use molecular dynamics simulation (see Figure 1) for wide range of temperatures ($T = 300 - 550$ K)

THEORY AND MODEL

Isotherm adsorption

The reaction between the gas phase and the adsorbed phase on the surface can be written:



At equilibrium, the gas chemical potential is equal to the surface chemical potential:

$$\mu_g = \mu_s \quad (2)$$

$$\mu_g = \mu_g^0 + RT \ln \left(\frac{p}{p_0} \right) \quad (3)$$

where μ_g^0 is the standard chemical potential of the gas phase, *i.e.*, the chemical potential at the reference pressure p_0 .

We may also write the chemical potential for surface as

$$\mu_s = \mu_s^* + RT \ln a_s \quad (4)$$

where a_a is the activity of the adsorbed phase:

$$a_s = \gamma \frac{C_s}{C_s^*} \quad (5)$$

where μ_a^* is the standard state chemical potential at standard state. It follows from equation 2 that

$$\mu_a^* - \mu_g^0 = RT \ln \left(\frac{p}{p^0 a_s} \right) \quad (6)$$

Hence the adsorption equilibrium constant is given by

$$K = \left(\frac{p^0 a_s}{p} \right) \quad (7)$$

If we choose the standard state such that $p^0 = 1 \text{ atm}$,

$C_s^* = C_s^{\text{max}}$ then we obtain the Langmuir model isotherm

$$\frac{C_s}{C_s^{\text{max}}} = \frac{Kp}{1 + Kp} \quad (8)$$

K is the Langmuir equilibrium constant. The van't Hoff relationship to describe the temperature dependence of K

$$K = K_0 \exp \left(\frac{-\Delta H^0}{RT} \right) \quad (9)$$

where K_0 is the pre-exponential factor, and ΔH^0 is the constant iso-steric enthalpy of adsorption. Plotting K semi logarithmically versus $1/T$ gives a linear fit from which the slope $-\Delta H^0 / R$ is extracted.

Surface Excess Densities

In a thermodynamic description, the surface excess concentration C_s is determined. From that we can describe the adsorption isotherm by plotting the surface excess density versus the gas pressure. We use the Gibbs surface excess for systems in global equilibrium as described in the book of Kjelstrup and Bedeaux.⁹ An interface is considered as a thin layer between phases. We restrict ourselves to surfaces parallel to the graphite surface, so

$$C_s = \int_{\alpha}^{\beta} (C^{2nd} - C^{gas}) dz \quad (10)$$

where C_s is the surface excess concentration, and C^{gas} , C^{2nd} are the concentration of CO_2 in the gas and in the second layer, respectively. (See Figure 2)

Simulation details

We performed classical molecular dynamic (MD) simulation with the DL_POLY classic package¹⁰ to understand the mechanism of CO_2 adsorption and transport on the graphite surface. The system consists of a sheet of crystalline graphite and CO_2 molecules. The graphite has hexagonal structure with P63/mmc without any defects. The crystal is constructed from 5 sheets of graphene and contains 4284 carbon atoms. We orient graphene sheets in our simulation box such that the surfaces of the sheets are perpendicular to the z direction. The size of the box is around $42 \times 51 \times 84 \text{ \AA}^3$. We use periodic boundary conditions in all directions. At least ten systems with different number of CO_2 molecules ranging from $N_{\text{CO}_2} = 50 - 700$ were

simulated. For each N_{CO_2} , simulations were performed at different 10 temperatures in the range 300-500K.

The MD simulation had time steps of 0.001ps. The initial configuration was constructed by randomly distributing of CO_2 molecules above the graphite surface. The system was stabilized during 1000 ps by NVT runs with the Nosé-Hoover thermostat.¹¹ When the system was in the thermal equilibrium, we performed another 1000 ps run with microcanonical ensemble (NVE) to study adsorption and transport properties. The trajectory is printed every 100 time step and stored for further analysis.

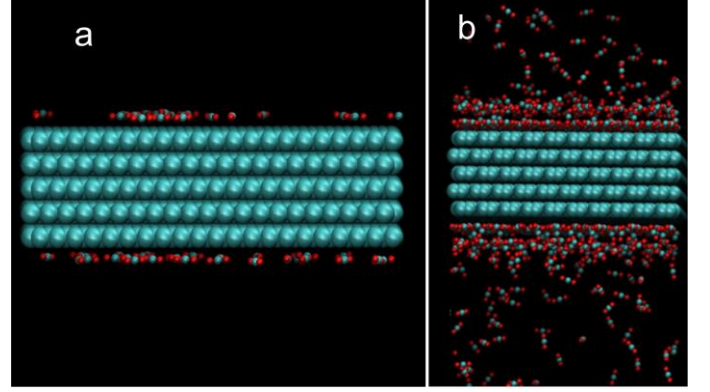


Figure 1. Typical snapshot of CO_2 adsorption on graphite surface at $T=350\text{K}$ with $N_{\text{CO}_2}=50$ (a) and $N_{\text{CO}_2}=600$ (b). In the time scale of simulation there is no CO_2 molecule in the gas phase at low concentration (a). At high concentration, there are two layers of CO_2 forming on the surface (b). The green, red are represented carbon and oxygen atom, respectively.

Potential energy interaction

We fix the graphite layer and use the rigid body model TraPPE for CO_2 .¹² The intermolecular potential consist of the long range Columbic interactions handled using the Ewald sum technique¹³ and the shifted and truncated 12-6 Lennard-Jones (LJ) potential.¹³

$$V_{ij}^{nb} = V_{ij}^{LJ} + V_{ij}^{columbic} \quad (11)$$

$$V_{ij}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (12)$$

$$V_{ij}^{LJ}(r_{ij}) = \begin{cases} V_{ij}(r_{ij}) - V_{ij}(r_c) & r_{ij} < r_c \\ 0 & r_{ij} > r_c \end{cases} \quad (13)$$

where r_{ij} is the distance between atoms i and j , ϵ_{ij} and σ_{ij} are LJ potential parameters, and r_{ij} is the cutoff radius. The LJ interaction parameters between different types of atoms are calculated from the Lorentz-Berthlot mixing rules¹³

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (14)$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad (15)$$

The parameters is taken from the DREIDING¹⁴ and TraPPE¹² force field are listed on table 1.

Table 1. LJ potential parameters used in simulation

Atom	σ (Å)	ϵ/k_B (K)	charge (e)
C (in CO ₂)	2.80	27	0.7
O (in CO ₂)	3.05	79	-0.35
C (graphite)	3.34	26	0

RESULTS AND DISCUSSION

Two distinct CO₂ surface layers

Figure 2 depicts the distribution of CO₂ molecules along the surface of graphite with system $N_{\text{CO}_2}=700$ at different temperatures. It is shown that there are different regions of CO₂ on the surface. The first adsorption layer is located around 0-5Å, the second adsorption layer is located around 5-12Å and the CO₂ gas above 12 Å. The first layer is well separable from the second, see bar indicated with α . The separation between the second layer and the gas β is less precise. In the first layer, there are two peaks, the higher one is big and corresponds to the CO₂ molecule that are parallel to the surface. The second small peak corresponds CO₂ molecules that do not touch completely the surface (the angle surface-C-O is around 30°).

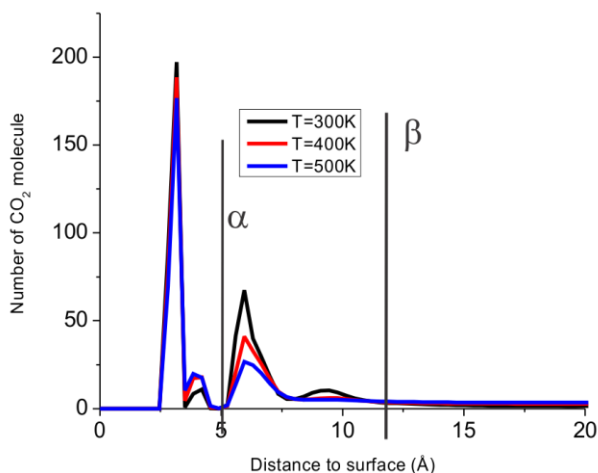


Figure 2. The distribution of CO₂ molecules along the surface in different layer with $N_{\text{CO}_2}=700$ at selected temperatures. There are three zones, from 0- α : first adsorbed layer, α - β : second adsorbed layer, above β : gas phase.

The radial distribution function (RDF) of CO₂-CO₂ molecules of the different layers along is reported in Figure 3. In the first adsorption layer (Nad1) the RDF of CO₂ has a liquid like form. Molecules are more organized than in the second layer (Nad2) and the gas phase (Ngas). The position of maximum RDF of the first layer is slightly below that of the second layer and the gas.

Figure 4 depicts the trajectories of CO₂ molecules during 100 ps. The lines indicate the motion of CO₂ during the trajectory. The first layer (dark color in Figure 4) does not exchange molecules with the second layer. Only CO₂ from the second layer go in and out of the gas phase (the blue lines in Figure 4). This behavior occurs during the whole simulation of 1000 ps.

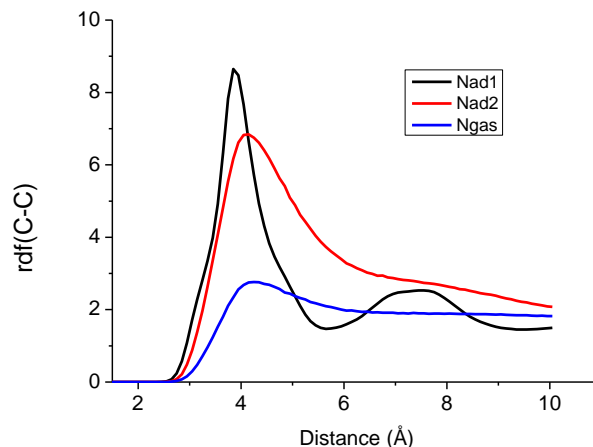


Figure 3. Radial distribution function of CO₂-CO₂ in different layers

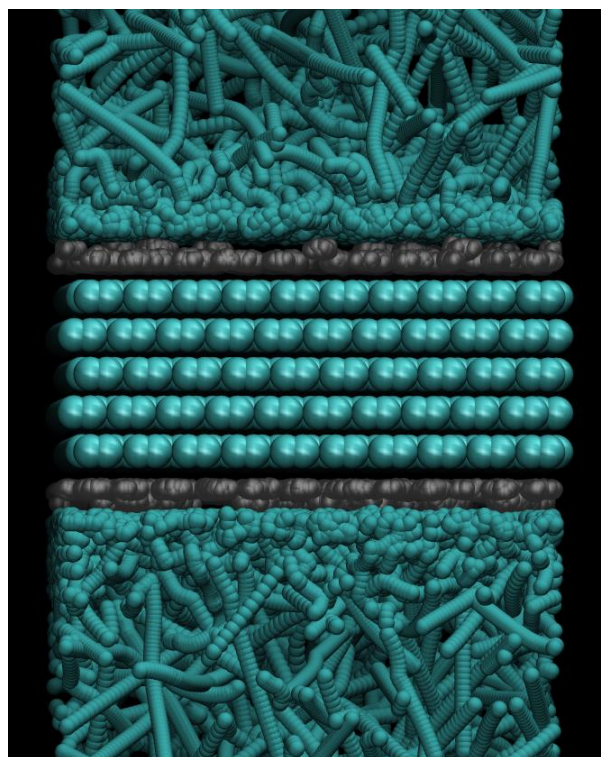


Figure 4. Trajectory plot of CO₂ movement in different layers in time scale of 100ps. Only carbon atom is shown. The dark color is the adsorbed first layer. There is only the second layer exchange molecule with gas phase.

The Langmuir model for the adsorption isotherm

In the previous section we have shown that the first layer and the second layer of adsorbed CO₂ show very different behavior. So we only use the second layer to construct the adsorption isotherm.

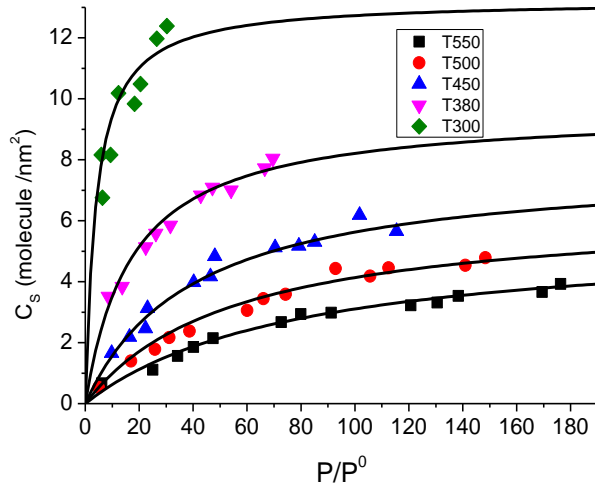


Figure 5. CO₂ adsorption isotherm on graphite surface at selected temperatures. The continuous line is the fitted Langmuir model.

Table 2. Langmuir parameters isotherm of CO₂ on graphite

T (K)	C_s^{\max} (molecule/nm ²)	K
300	13.2	2.48×10^{-1}
320	12.2	1.53×10^{-1}
350	10.5	1.08×10^{-1}
380	9.6	5.74×10^{-2}
400	9.1	4.57×10^{-2}
420	8.7	3.65×10^{-2}
450	7.9	2.49×10^{-2}
480	6.8	2.06×10^{-2}
500	6.4	1.82×10^{-2}
550	5.6	1.27×10^{-2}

The Langmuir model can be fitted quite well to experimental adsorption isotherms for CO₂ on activated carbon.² We extended the number of CO₂ molecules to 2000 in an additional calculation to see if we could obtain more than two adsorbed layers. However the system formed only two layers as in Figure 2. The Langmuir model was chosen to fit our data. The isotherms are presented in Figure 5. The excess surface adsorption of the second layer reaches a plateau when the pressure increases. This type of adsorption is typically for a CO₂ isotherm not only on graphite, activated carbon but also on other material such as zeolite, MOF, COF, etc.

The parameters for Langmuir equation 8 are presented in Table 2. The maximum excess adsorption decreases when the temperature increases (Figure 6).

A plot of the logarithm of the equilibrium constant K versus the inverse temperature is given in Figure 7. The dependence is linear and from the slope, a value of the isosteric enthalpy of adsorption $\Delta H^0 = -16$ kJ/mol is obtained. This value is typical for physisorption and in the range (-10.5, -28.4 kJ/mol) of experimental data of adsorption of CO₂ on activated carbons.^{3,7,15}

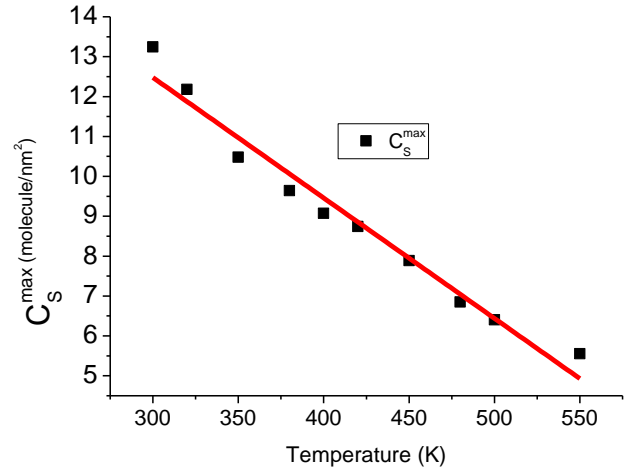


Figure 6. Maximum excess surface adsorption as a function of temperature

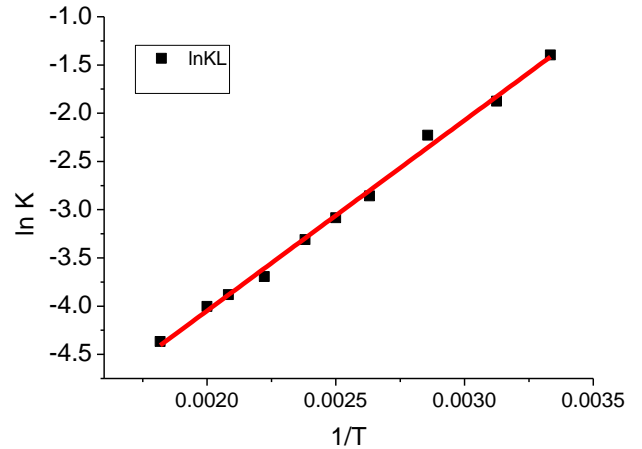


Figure 7. Logarithm of the adsorption equilibrium constants versus the inverse temperature for adsorption of CO₂ on graphite

Surface self-diffusion

We limited our study to the self-diffusion of adsorbed CO₂ on the surface. This gives an important contribution to the transport of CO₂ inside the slit pores. The self-diffusion coefficient of molecule can be obtained from:

$$D_{||}^s = \lim_{t \rightarrow \infty} \left[\frac{1}{2dNt} \sum_{i=1}^N \left\langle \left| \vec{r}_i(t) - \vec{r}_i(0) \right|^2 \right\rangle \right] \quad (16)$$

where d is the dimensionality (for surface $d = 2$), N is the total molecules, $\vec{r}_i(t)$ and $\vec{r}_i(0)$ is the position of molecule at time t and time initial.

By plotting the logarithm of the diffusion coefficients found versus the inverse of temperature, we obtained an Arrhenius plot. This was used to estimate the temperature dependence of the diffusion coefficient according to

$$D(T) = D_0 \exp\left(\frac{-E_{\text{act}}}{k_B T}\right) \quad (17)$$

where D_0 is the pre-exponential factor, k_B is the Boltzmann constant, and E_{act} is the activation energy.

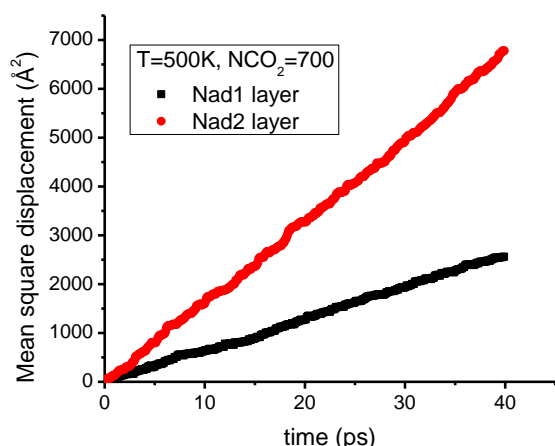


Figure 8. The mean-squared displacement of CO₂ in the first and second layer at T=500K and NCO₂=700

Figure 8 shows an example of mean-squared displacement of CO₂ in the first layer and in the second layer. It is clearly shown that CO₂ in the first layer also mobile but slower.

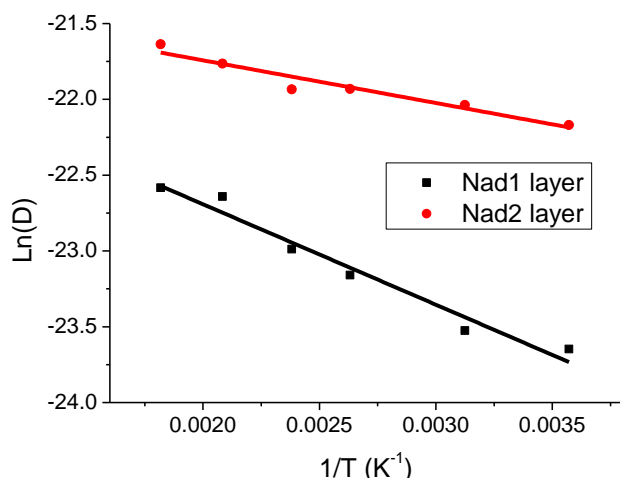


Figure 9. Natural logarithm of the self-diffusion coefficients as a function of inverse temperature.

The activation barrier for self-diffusion is obtained by calculating the slope of linear relationship between the natural logarithm of self-diffusion and $1/T$ (Figure 9). We found that for the activation barriers of the first and second layer were $E_{act1}=5.5$ and $E_{act2}=2.3$ kJ/mol, respectively.

Along the graphite surface, the diffusion coefficient of first and second layers of CO₂ on graphite surface is roughly 10^{-11} m²/s and 10^{-10} m²/s, respectively which are in good agreement with previous simulations.^{8,16} The value is much smaller than for diffusion of H₂ on graphite (10^{-7} m²/s). It is interesting that the first layer of adsorbed CO₂ is mobile along the surface. The mobility is less than that of the second layer because the first layer is confined between graphite surface and the second layer and has a strong interaction with the graphite surface. The figure is comparable with the picture of mobile H₂ molecule on graphite by Simon *et al.*^{17,18}

CONCLUSION

In this work, we have used Equilibrium Molecular Dynamics to study the adsorption isotherm and diffusion of CO₂ on a graphite surface. The results show that there are two CO₂ adsorbed layers. The two layers have very different diffusion and exchange possibilities with the gas phase. A simple Langmuir model was used to fit the isotherm of the second layer. The heat of adsorption was estimated ($\Delta H^0 = -16$ kJ/mol). The rate of self-diffusion of CO₂ on graphite ($\sim 10^{-10}$ m²/s) is small compared to H₂ adsorbed ($\sim 10^{-7}$ m²/s) and CO₂ dense gas ($\sim 10^{-9}$ m²/s). These results of the equilibrium system form the basis for further studies of non-equilibrium properties of pure CO₂ and mixture CO₂/H₂ systems.

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