

Gas adsorption on the surface of aerosol particles. Results of laboratory and field experiments

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Heterogeneous processes on carbon and carbonaceous aerosols are considered. The results of a laboratory study of the accommodation factor (adsorption factor) of nitrogen dioxide on the surface of carbon fibers and calculated values of this factor for soot particles are presented. It is shown that adsorption of nitrogen dioxide on hydrophobic carbon and hydrophilic soot strongly depends on the atmospheric humidity.

Introduction

Atmospheric aerosols take part in the ozone cycles in two ways. In addition to the direct participation of the particle surface in heterogeneous accommodation of the particle surface in heterogeneous accommodation of ozone,¹ aerosols can adsorb low-activity trace gases and increase their chemical activity.² Such gases are activated upon the interaction with the surface and thus initiate heterogeneous reactions of ozone destruction. It is especially important to study heterogeneous processes on aerosols produced at combustion, that is, various types of soot. These aerosols are the most widespread type of anthropogenic aerosols. Depending on the specific surface area of aerosol particles, the content of carbon in them, and hydrophilicity they can adsorb trace gases in different ways. In the previous Ref. 3 it has been shown that the mass accommodation factor of watered soot can achieve 0.1.

This paper presents the results of laboratory modeling of physical adsorption of some gases along with the calculated results on the mass accommodation constants of these gases on the surface of carbonaceous aerosol particles obtained using data of field experiments.

Model of the process

In simulation, the following assumptions are accepted:

a) a gas molecule, accommodated on the sorbent surface, occupies the area σ , which cannot be used for accommodation of other molecules;

b) the accommodation factor k_{ac} is defined as a probability of adsorption of a gas molecule by a free part of the sorbent surface.

The energy interaction of the adsorbed gas molecules with each other is ignored. It is postulated that the gas concentration is the same everywhere in the vessel volume and no diffusion restrictions exist.

The change in the pressure of gas molecules per unit time is

$$\frac{dp}{dt} = -k_{ac}a \frac{S}{V} p + k_{ac}a\sigma \frac{N_A}{RT} (p_0 - p)p + k_{des}(p_0 - p), \quad (1)$$

where $a = (kT/2\pi m)^{1/2}$ (k is the equilibrium constant; m is the mass of one molecule); S is the sorbent surface; V is its volume; σ is the effective area of a molecule; N_A is the Avogadro number; R is the absolute gas constant.

The first term of the sum is responsible for the rate of adsorption of gas molecules by the free (not occupied) surface, the second and the third terms are responsible, respectively, for the decrease in the adsorption rate as the sorbent surface is occupied by gas molecules and for the desorption rate.

As the equilibrium is established ($p = p_{eq}$), the equality (1) tends to zero, whence

$$\frac{p_{eq}}{p_0 - p_{eq}} = \frac{k_{des}V}{k_{ac}aS} + \frac{V\sigma N_A}{S RT} p_{eq}. \quad (2)$$

Changing the initial gas pressure and, correspondingly, the equilibrium pressure, it is possible to construct the dependence $p_{eq}/(p_0 - p_{eq}) = F(p_{eq})$, which must be linear, provided that the model is adequate. The slope of thus obtained straight line is

$$(V\sigma N_A)/(SRT), \quad (3)$$

and the intercept is

$$(k_{des}V)/(k_{ac}aS).$$

From the slope of the obtained straight line, we can calculate S/σ (the maximum possible number of gas molecules accommodated as a monolayer on the sorbent surface and corresponding to $\theta = 1$, where θ is the degree of occupation of the sorbent surface). Having known σ , it is possible to determine the sorbent surface area S . Using this value, we can calculate the ratio k_{des}/k_{ac} and k_{ac} from the intercept value.

Results of laboratory modeling

In the experiments, we have studied the kinetics of variation of the dichlorethane vapor and NO_2 pressure

in the process of their sorption on the surface of a carbon fiber with the specific surface area <math> < 2 \text{ m}^2/\text{g}</math>.

The time dependences of variation of the dichlorethane vapor and NO₂ pressure, transformed in accordance with Eq. (2), are shown in Figs. 1 and 2.

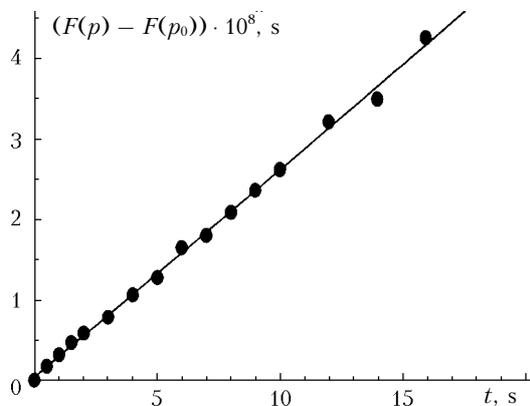


Fig. 1. Time dependence of $F(p) - F(p_0)$; $T = 293 \text{ K}$.

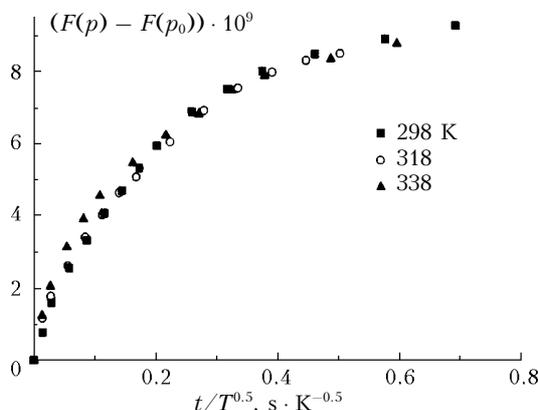


Fig. 2. The $(F(p) - F(p_0))$ difference as a function of time normalized to the particle speed.

The results obtained were used to calculate the accommodation factor of dichlorethane on the graphite surface $k_{ac} = (6.1 \pm 0.3) \cdot 10^{-9}$ and the factor of desorption $k_{des} = (8.8 \pm 1.6) \cdot 10^{-2} \text{ s}^{-1}$ at $T = 293 \text{ K}$.

The kinetic sorption factors of NO₂ were calculated in a similar way. However, the transformed dependence was not linear. This is likely connected with the fact that nitrogen dioxide in the gaseous state is a mixture of NO₂ and its dimer N₂O₄ and, thus, in this case the accommodation involves two types of molecules with different mass and speed. The factor k_{ac} amounted to about $2 \cdot 10^{-9}$ at the initial parts of the curves (at the time $t < 1 \text{ s}$) and decreased to $2 \cdot 10^{-10}$ at the later stages, for which k_{des} had the following values:

Table

$T, \text{ K}$	$k_{des} \cdot 10^5, \text{ s}^{-1}$	Standard error, $\text{s}^{-1} \cdot 10^5$
298	2.8	0.14
318	3.3	0.16
338	3.7	0.18
353	4.1	0.22

Model for calculation of the NO₂ accommodation factor based on data of field experiments

To calculate the factor of accommodation of nitrogen dioxide on aerosol particles based on experimental data, the simplified equation for the average (over volume) NO₂ concentration n is usually used¹:

$$\frac{dn}{dt} = \Delta q - \frac{n\bar{v}}{4} S\gamma. \tag{4}$$

This equation involves the emission rate of volume sources and the NO₂ sink Δq , the total surface of aerosol particles in the unit volume S , the probability of trapping molecules on the surface of aerosol particles (accommodation coefficient) γ , and the mean thermal speed of molecules $\bar{v} = \sqrt{8RT/(\pi m)}$. It is assumed that the flow of active molecules onto the aerosol particles is determined by the well-known gas-dynamics equation, which is valid at the large Knudsen numbers and arbitrary γ or at $\gamma \ll 1$ and arbitrary Knudsen numbers.

To describe the size distribution of aerosol particles, the Modal Aerosol Dynamics Model for Europe (MADE) is usually applied,⁴ in which the particle size distribution is presented in the three-mode form. Each of the modes, namely, nucleation, condensation, and the coarse one, is approximated by a lognormal function. However, in some cases, either a unimodal lognormal distribution (LND)⁵ or a unimodal modified gamma distribution (GD)⁶ is also used.

In the calculation, we used the experimental values of the number concentration of aerosol particles with diameters of 0.042–0.237 μm . This mode of the particle size distribution is described by the lognormal function.

For spherical particles with the radius r , the particulate matter density ρ , the number concentration N_0 , and the rate of trapping of NO₂ molecules on the particle surface can be expressed through the number concentration as follows:

$$-\frac{dn}{dt} = n\bar{v}\pi N_0\gamma \int_0^\infty r^2 f(r) dr, \tag{5}$$

whence

$$\gamma = -\frac{1}{\pi\bar{v}nN_0} \frac{1}{\int_0^\infty r^2 f(r) dr} \frac{dn}{dt}. \tag{6}$$

Calculated results

To calculate the factor of nitrogen dioxide accommodation on aerosol particles, we considered the data of the experiments conducted in the 15-km long plume of soot smog generated by a forest fire. In this period correlation was observed between the increase in the aerosol number concentration and the decrease in the NO₂ concentration, against the

background of convective transport (temperature increase by 15 degrees and humidity decrease by 20%). The indication of this were the fluctuations of the NO₂ and aerosol content, which manifested themselves regardless of the diurnal behavior caused by the vertical transport and the turbulent diffusion.

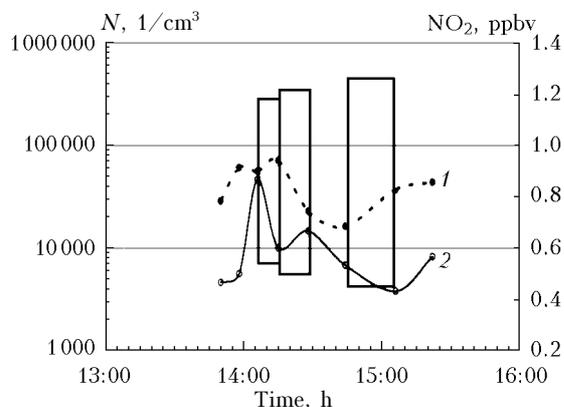


Fig. 3. Temporal behavior of aerosol (1) and NO₂ (2); TROICA-5 (July 1, 1999).¹

In this experiment, the data were collected that are characteristic of NO₂ sink onto the aerosol particles

($\Delta q = 0$). Significant fluctuations of the aerosol and NO₂ concentrations were analyzed (Fig. 3).

The results of analysis of the kinetic curves of the NO₂ and aerosol concentration, as well as the estimates of the NO₂ accommodation factor (γ) are presented in the Table.

Discussion and conclusions

We have compared the nitrogen dioxide accommodation factor values obtained based on the data of field and laboratory experiments.

It has been shown that laboratory experiments on the nitrogen dioxide adsorption on the carbon fiber give the accommodation coefficient values, which are several orders of magnitude lower than those in the field experiments for the anthropogenic soot particles.

This is likely explained by the fact that the increase of the specific surface area of a carbonaceous sorbent leads not only to the increase of the NO₂ accommodation factor, but also to the increase of the sorbent hydrophilic properties, the increase of water accommodation factor, and, ultimately, to the strong watering of particles.

Table

Time period	$\langle T \rangle$, °C	$\langle T \rangle$, K	$\langle v_{\text{NO}_2} \rangle$, m/s	$\langle n_{\text{NO}_2} \rangle$, ppbv	$\langle n_{\text{NO}_2} \rangle$, kg/m ³	$\langle N_0 \rangle$, 1/m ³
14:06:00–14:15:00	31.84	304.84	545.0045	0.68	$1.2854 \cdot 10^{-9}$	$55926 \cdot 10^{-6}$
14:15:00–14:28:00	31.775	304.775	544.9463	0.73	$1.3794 \cdot 10^{-9}$	$71122 \cdot 10^{-6}$
14:28:00–15:06:00	31.33	304.326	544.545	0.54	$1.0241 \cdot 10^{-9}$	$16278 \cdot 10^{-6}$
Time period	Δt , min	Δt , s	$\Delta n(\text{NO}_2)$, ppbv	$\Delta n(\text{NO}_2)$, kg/m ³	$\frac{\Delta n}{\Delta t}$, kg/(m ³ ·s)	k_{ac}
14:06:00–14:15:00	0:09:00	540	0.37	$6.9 \cdot 10^{-10}$	$1.2772 \cdot 10^{-12}$	$-3.0 \cdot 10^{-2}$
14:15:00–14:28:00	0:13:00	780	0.27	$5.02 \cdot 10^{-10}$	$6.4308 \cdot 10^{-13}$	$-1.1 \cdot 10^{-2}$
14:28:00–15:06:00	0:22:00	1320	0.23	$4.39 \cdot 10^{-10}$	$3.325 \cdot 10^{-13}$	$-3.3 \cdot 10^{-2}$

Notes. $\langle T \rangle$ is the mean temperature of air for the given period; $\langle v \rangle$ is the mean speed of NO₂ molecules; $\langle n \rangle$ is the mean concentration of NO₂; N_0 is the number concentration of aerosol particles.

Acknowledgments

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