Distribution functions of adsorption sites on the surface of stainless steel during water vapor adsorption

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ABSTRACT

Adsorption methods for determining the properties of stainless steel surface are presented. The relation between the actual and geometric surface is determined. The dependence of adsorption heat on the coverage logarithm is derived from experimental adsorption isotherms for water at 298 K. On the basis of this dependence, differential and integral distribution functions of adsorption sites by adsorption heat is calculated. It is shown that in the case of water adsorption on the surface of stainless steel at 298 K, adsorption heat for 90% of adsorption sites ranges from 4.4×10^7 to 7.9×10^7 J/kmol.

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1. Introduction

The structural and energetic properties of the surface play an important part in the development of vacuum coating processes, examination of friction, adhesion, and emission of charged particles, material outgassing, and analysis of the non-stationary modes of operation of vacuum installations [1–7]. Experimental investigation of water vapor adsorption on stainless steel makes it possible to obtain adsorption isotherms [2,3]. Besides, their adaptation using adsorption theories allows determining some of the properties of the surface, actually adsorbent surface and average adsorption heat. Study [1] attempts to calculate numerically the distribution of adsorption sites by adsorption heat from pumping curves based on the Langmuir adsorption isotherm equation. But the Langmuir isotherm does not suit for this purpose.

This study proposes an analytical method of determining the distribution functions of adsorption sites by adsorption heat based on the Freundlich adsorption isotherm equation.

2. Adsorption isotherms

Adsorption isotherms are often used to determine properties of porous adsorbents: zeolites, activated carbons, silica gels, etc.

Determining small quantities of an adsorbate is rather complicated on smooth, non-porous surfaces, particularly in a vacuum.

Study [2] uses a volumetric method for determining adsorption isotherms in order to examine the water vapor adsorption on the stainless steel at 298 K. The Freundlich equation

$$a = d \cdot p^m, \tag{1}$$

where a is the quantity of gas adsorbed on an area unit of geometric surface, m^3Pa/m^2; p is pressure, Pa; $m = 0.345$, $d = 0.018$ are experimentally determined constant coefficients in the pressure range 10^{-1}–2.10^1 Pa.

The Brunauer-Emmett-Teller (BET) equation:

$$\frac{p/p_0}{a(1 - p/p_0)} = \frac{1}{C \cdot a_m} + \frac{(C - 1) \cdot p/p_0}{C \cdot a_m}, \tag{2}$$

where p_0 is saturated vapor pressure, Pa; a_m is the quantity of gas absorbed in a monolayer on a unit of geometric surface area, m^3Pa/m^2; $C = \exp[(Q_m - E)/RT]$, where Q_m is the average adsorption heat in the first layer, J/kmol; E is adsorbent condensation heat at 298 K; T is temperature, K; $R = 8.31 \times 10^3$ J/(K.kmol). Equation (2) is valid for water at 298 K in the pressure range 16.8−630 Pa when $C = 86.4$, $a_m = 0.116$ m^3Pa/m^2 and the average water molecule adsorption heat in the first layer $Q_m = 5.5.10^7$ J/kmol [2].

Study [3] uses a constant pressure method to determine water

vapor adsorption at 298 K on the electropolished stainless steel.

3. Pump-down curves

Freundlich adsorption isotherm coefficients can also be determined using the model of pump-down characteristics of vacuum chambers with adsorbing walls [5] by backward calculations from pump-down curve equations for a regular mode. This equation produces a dependence of pressure on a pump-down time in as follows:

$$p(t) = \left[\frac{d \cdot m \cdot F}{3600 \cdot S(1-m) \ t} \right]^{\frac{1}{1-m}}, \tag{3}$$

where F is the geometric surface area, m^2; S is the effective pumping speed of vacuum chamber, m^3/s; t is pump-down time, h; m and d are Freundlich adsorption isotherm coefficients.

Experimental pump-down curves in the regular mode may be described in as follows:

$$p(t) = A_1 t^{-B}, \tag{4}$$

Where $A1$ and B are constant experimental coefficients which permit to find Freundlich adsorption isotherm coefficients. From (3) and (4) if $f = F/S$, then follows:

$$d = 3600 \frac{(1-m) \cdot \cdot A_1^{1-m}}{m \cdot f}, \quad m = \frac{B-1}{B}.$$

Table 1 shows the experimentally determined Freundlich equation coefficient m for water on the stainless steel at 298 K.

4. Surface properties

The BET adsorption isotherm (2) makes it possible to determine the values of constants $C = 86.4$ and $a_m = 0.116$ m^{3}Pa/m^2. With water condensation heat $E = 4.4.10^7$ J/kmol, the average water molecule adsorption heat in the first layer $Q_m = 5.5.10^7$ J/kmol [2]. The dependence of the surface coverage on pressure can be calculated using the combination of data from equations (1) and (2) (Fig. 1).

The experimentally determined value of the monomolecular coverage makes it possible to calculate the relation between the area of actual and geometric surface. A unit of actual surface with the monomolecular coverage $a_m = 0.116$ m^{3}Pa/m^2 exists $N_m = 2.82 \times 10^{19}$ adsorption sites. A unit of the monomolecular coverage of the smooth surface can exists $N_1 = 4.9.10^{18}$ water molecules. Thus, the actual adsorbent surface is $N_m/N_1 = 5.8$ times larger than the geometric surface.

The average water molecule adsorption heat in the first layer $Q_m = 5.5.10^7$ J/kmol derived from the BET equation does not provide a sufficient indication of the energy properties of the surface, which can be obtained by analyzing the density distribution of adsorption sites by adsorption energy. Study [1] attempts to obtain such distribution from pumping curves using a numerical method.

Table 1
Coefficient "m" in Freundlich isotherm equation.

No.	Preliminary treatment	m	Reference
1[a]	untreated	0.34	[2]
2[b]	electropolishing	0.25	[3]
3[b]	chemical etching	0.23	[5]
4[b]	electropolishing	0.29	[6]

[a] Calculated from adsorption isotherms.
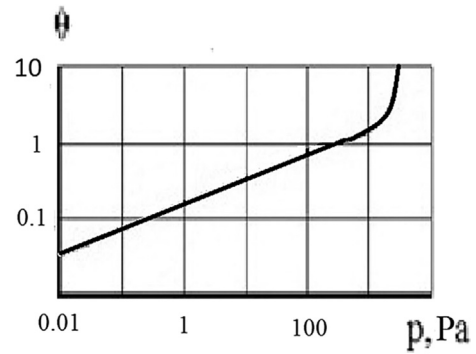[b] Calculated from pump-down curves.

Fig. 1. Surface coverage with water molecules of untreated stainless steel X18H9T at 298 K.

However, adsorption isotherms in pump-down curve equations are described using the Langmuir isotherm equation. The Langmuir isotherm equation assumes saturation at $\theta = 1$, which contradicts the experimental data (Fig. 1).

A lack of saturation at $\theta = 1$ indicates that adsorption takes place both on free and occupied sites, while migration ensures molecule transfer on the surface between the adsorption sites with different adsorption heat, first filling the sites with the maximum adsorption heat. With this assumption, let us make a search for an analytical representation of the distribution function of adsorption sites by adsorption heat.

The molecular-kinetic theory suggests that the equilibrium state of adsorbed gas corresponds to the equal rate of evaporation and condensation of molecules on the surface of a solid body.

$$\frac{a}{\tau} = K \cdot p \tag{5}$$

where K is a proportionality coefficient, m^{3}Pa/(s.Pa), and τ is adsorption time. For heterogeneous surfaces, as the exponent of τ in (5) is equal to unity. τ is mean adsorption time for all adsorption sites having different adsorption heat.

$$K = \frac{\gamma \cdot 6,02 \cdot 10^{26}}{2.43 \cdot 10^{20} \sqrt{2\pi MRT}} = \frac{1,1 \cdot 10^4 \cdot \gamma}{\sqrt{M \cdot T}}, \tag{6}$$

where M is the molecular mass of gas, kg/kmol; γ is condensation probability. Adsorption time τ can be calculated using Frenkel's formula [8]

$$\tau = \tau_0 \exp\left(\frac{Q_a}{R \cdot T} \right). \tag{7}$$

where $\tau_0 = 1.6 \cdot 10^{-13} \frac{298}{T}$.

Freundlich equation (1) and kinetic equation (5) can both be valid for any pressures, providing that on the surface there are adsorption sites with different adsorption heat Q_a.

$$\begin{cases} a = d \cdot p^m, \\ a = \tau \cdot K \cdot p. \end{cases} \tag{8}$$

In system (8) τ is the mean adsorption time for all occupied sites. The dependence of the adsorption heat on the surface coverage can be derived from condition (8) through mathematical transformations (Appendix P1).