



# A numerical solution of density distribution function of water adsorption sites on vacuum technical metal surfaces



Detian Li, Yongjun Cheng, Yanwu Li\*, Lan Zhao, Wenjun Sun, Yongjun Wang

Science and Technology on Vacuum Technology and Physics Laboratory, Lanzhou Institute of Physics, PO Box 94, Lanzhou 730000, PR China

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## ABSTRACT

During the pump-down process of technical metal vacuum systems without bakeout after air exposure, water makes up most of the desorbed gas in a short term. The desorbed water comes from the near-surface regions (inside the oxide layers and their surfaces) of the vacuum metal materials. If the thickness of the oxide layer is very small, and the surface is smooth, then the outgassing will be dominated by the mechanism of adsorption and desorption of water on the surface, and the molecular diffusion inside the oxide layer could be negligible. In some previous works, different isotherms were used to predict the pump-down curves, and to understand the mechanism of adsorption and desorption of water on the surfaces. The theoretical results with adjusted parameters often agreed well with the experimental phenomena. However, using these isotherms with known distributions to express the unknown densities of adsorption sites with different binding energies is an a priori method. In the present work, a numerical method is proposed to obtain a solution of density function of surface adsorption sites from the experimental data of pump-down reported by Edwards [J. Vac. Sci. Technol. 14, 606 (1977)].

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## 1. Introduction

Vacuum systems are widely used in many modern industries, from preparation of solid films to nuclear physics. During the pump-down process of unbaked vacuum systems made of metal after air exposure, water makes up most of the desorbed gas in a short term (~20 h) [1,2]. In addition, the outgassing rates of materials are often measured in metal vacuum system [3–5]. Redhead's work indicates that the measured values are invalid if the sticking probabilities of gases on the surface are not negligible [6]. To pump down rapidly and to measure the real material outgassing rates, the interactions between water molecules and metal surfaces need to be studied.

The desorbed water comes from the near-surface regions (inside the oxide layers and their surfaces) of the vacuum metal materials [7–10]. In the literature, two main theories have been developed in order to model water desorption: one based on the diffusion-limited model [1,11–13] and the other described by the adsorption and desorption equations on the surface [2,14–21]. The first one assumes that molecules diffuse along the pores or the grain boundaries of the oxide layer, and the desorption rate on the

surface is so quick that the outgassing rate is dominated only by the diffusion rate. The latter one assumes that the molecular diffusion is negligible, and the outgassing rate is governed solely by the molecular adsorption and desorption on the surface of the metallic oxide.

A complete theory composed of both diffusion and adsorption/desorption is complex. For the surface model theory, Horikoshi [14] has given the fundamental equations to obtain a physical understanding of desorption during pump-down. Based on Horikoshi's work, Kanazawa [15] has given the description of the quasi-steady-state condition with the assumption of constant sticking probability on empty sites. With this quasi-steady-state law, Redhead [2] has obtained the  $p-t$  curve of pump-down using different adsorption isotherms (Langmuir isotherm, Freundlich isotherm, Temkin isotherm, and extended Temkin isotherm). The extended Temkin isotherm gives  $p = p_0 t^{-\gamma}$  (where  $\gamma$  is about 1), which is in good agreement with the experimental phenomena. However, using these isotherms with known distributions to express the real densities of adsorption sites with different binding energies is an a priori method. In the present work, a method based on the fundamental equations of Horikoshi and Kanazawa is proposed to obtain a solution of density function of surface adsorption sites from the  $n-t$  (or  $p-t$ ) curve of pump-down. The pump-down curve used to cross check our theory comes from the experiment of Edwards [22].

\* Corresponding author.

E-mail address: [andersonliyanwu@sina.com](mailto:andersonliyanwu@sina.com) (Y. Li).

## 2. Numerical method

The pump-down of a metal vacuum vessel through an orifice or a valve with a known conductance is often used as a method to measure its own outgassing rate. In the experiment of Edwards, a valve was used [22]. The desorption rate of multilayer water is approximately constant, it can be considered as zero-order [23]. Given the low latent heat of vaporization, this process takes only a few seconds [16]. Thus, only the monolayer water needs to be considered during the pump-down. To solve the fundamental equations given by Horikoshi and Kanazawa, two main assumptions are as follows: (1) the sticking probability of water on the empty sites of metal surface (stainless steel, or aluminum alloy) is a constant value, and it will not change with the binding energy; (2) water desorbs not via the recombination of two hydroxyl groups, namely, the desorption can be considered as first-order [23].

### 2.1. Fundamental equations

In this section we will introduce the fundamental equations developed in Ref. [15]. For one monolayer adsorption of water (see equation (1a) of Ref. [15])

$$\int g(E)dE = \sigma_0 \quad (1)$$

where  $g$  is the density distribution function of adsorption sites per unit area;  $E$  is the activation energy of desorption;  $\sigma_0$  is the number of total adsorption sites per unit area, and it is in the order of  $\sim 10^{15}$  molecules/cm<sup>2</sup> [14,22].

The net outgassing rate  $I_{\text{net}}$  from the surface is

$$I_{\text{net}} = I_d - I_r = -A_s \int \frac{d\theta(t, E)}{dt} g(E)dE \quad (2)$$

where  $I_d$  is the desorbed gas stream, and  $I_r$  is the readsorbed stream;  $A_s$  is the total inner surface area of the vessel;  $\theta(t, E)$  is the occupied probability of the sites with energy  $E$ , it satisfies the equation (see Eq (3) of Ref. [15]).

$$\frac{d\theta(t, E)}{dt} = n\Gamma(T)c_0(T) \frac{1 - \theta(t, E)}{\sigma_0} - \frac{\theta(t, E)}{\tau(E)} \quad (3)$$

where  $n$  is the number density of gas phase molecules with temperature  $T$  of the surface;  $\Gamma$  is the average thermal velocity of gas phase molecules times 1/4;  $c_0$  is the sticking probability of a molecule on empty sites;  $\tau$  is the mean residence time of adsorbed molecules on a solid surface, it is

$$\tau(E) = \tau_0 \exp(E/RT) \quad (4)$$

where  $R$  is the gas constant, it is  $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ .

When  $d\theta(t, E)/dt = 0$ , the equilibrium solution of  $\theta$  derived from Eq. (3) is (see Eq (5) of Ref. [15]).

$$\theta_{\text{eq}}(E, n) = \frac{n\Gamma c_0 \tau / \sigma_0}{n\Gamma c_0 \tau / \sigma_0 + 1} \quad (5)$$

Using  $\theta_{\text{eq}}$  instead of  $\tau$ , Eq. (3) is rewritten as (see Eq (6) of Ref. [15]).

$$d\theta(t, E) = \frac{n\Gamma c_0}{\sigma_0} \frac{\theta - \theta_{\text{eq}}}{\theta_{\text{eq}}} dt \quad (6)$$

The true source of gas desorption is  $d\theta(t, E)$  (or rewritten as  $\Delta\theta(\Delta t, E)$  for numerical calculations). As proved in Appendix A,  $\Delta\theta(\Delta t, E)$  peaks at  $n\Gamma c_0 \tau / \sigma_0 = 1$  ( $\theta_{\text{eq}} = 0.5$ ). This means that during

pumping down, the outgassing rate is mainly dominated by molecules desorbing from adsorption sites with a binding energy around the energy  $E_n$

$$E_n = RT \ln(\sigma_0 / n\Gamma c_0 \tau_0) \quad (7)$$

where  $E_n$  is derived from  $n\Gamma c_0 \tau / \sigma_0 = 1$  and Eq. (4). According to Eq. (7), if  $n$  decreases to  $n/10$  or increases to  $10n$ ,  $E_n$  will increase or decrease by  $RT \ln(10)$ , respectively. Eq. (7) also gives

$$n = \frac{\sigma_0}{c_0 \Gamma \tau_0} \exp(-E_n/RT) \quad (8)$$

In this study,  $\sigma_0/c_0$  is taken as  $2 \times 10^{16}$  molecules/cm<sup>2</sup>. Table 1 shows the main parameters calculated with Eqs. (4) and (8). It can be seen that the mean residence time  $\tau$  changes from microseconds at 42 kJ/mol to hours at 94 kJ/mol; and the pressure  $p$  ( $p = nkT$ ) changes from  $\sim 10^3$  Pa at 42 kJ/mol to  $\sim 10^{-8}$  Pa at 102 kJ/mol.

### 2.2. A numerical solution of density function of adsorption sites

The experimental data of pump-down often fluctuate; this may be due to the measurement uncertainty. Thus, the experimental data should be firstly fitted with a polynomial equation in exponent coordinates. Secondly, the fitted pump-down curve ( $n - t$ ) is divided into  $M$  elements according to Eqs. (7) and (8) with equal energy interval  $\Delta E$  as follows

$$n_{i+1}/n_i = \exp(-\Delta E/RT) \quad (9)$$

where  $i = 1, 2, 3, \dots, M$ ;  
and

$$\Delta E = (E_{\text{end}} - E_{\text{start}})/M \quad (10)$$

where  $E_{\text{start}} = RT \ln(\sigma_0/n_{\text{start}}\Gamma c_0 \tau_0)$  and  $E_{\text{end}} = RT \ln(\sigma_0/n_{\text{end}}\Gamma c_0 \tau_0)$ ;  $n_{\text{start}}$  and  $n_{\text{end}}$  are the values of  $n$  at the start and the end points of the pump-down curve, respectively. The range of activation energies  $E$  of density function  $g(E)$  is from  $E_{\text{min}}$  to  $E_{\text{max}}$ , and is divided into  $N$  elements with equal interval  $\Delta E'$ .

$$\Delta E' = (E_{\text{max}} - E_{\text{min}})/N \quad (11)$$

where  $E_{\text{min}} = E_{\text{start}} - RT \ln(10)$  and  $E_{\text{max}} = E_{\text{end}} + RT \ln(10)$ . The energy span is expanded by  $RT \ln(10)$  at the start and the end points, respectively. This will be explained later in Section 3.

Eq. (2) can be rewritten as follows for numerical calculations

$$\begin{aligned} (I_d - I_r) \Delta t_i &= -A_s \sum_{j=1}^N \Delta\theta(\Delta t_i, E_{j,1/2}) g(E_{j,1/2}) \Delta E' \\ &= I_{p,1/2}(t_i) \Delta t_i + V \Delta n(t_i) \end{aligned} \quad (12)$$

**Table 1**

Main parameters.  $p = nkT$  and  $n = \sigma_0/\Gamma c_0 \tau$ , where  $k$  is the Boltzmann constant,  $T = 295 \text{ K}$ ,  $\tau_0 = 10^{-13} \text{ s}$ ,  $\Gamma = 147.3 \text{ m/s}$ , and  $\sigma_0/c_0 = 2 \times 10^{16}$  molecules/cm<sup>2</sup>.

$E_n$ (kJ/mol)	$\tau$ (s)	$p$ (Pa)	$n$ (m <sup>-3</sup> )
42	$2.73 \times 10^{-6}$	$2.02 \times 10^3$	$4.97 \times 10^{23}$
50	$7.13 \times 10^{-5}$	$7.76 \times 10^1$	$1.90 \times 10^{22}$
58	$1.86 \times 10^{-3}$	2.97	$7.30 \times 10^{20}$
66	$4.85 \times 10^{-2}$	$1.14 \times 10^{-1}$	$2.80 \times 10^{19}$
74	1.27	$4.37 \times 10^{-3}$	$1.07 \times 10^{18}$
82	$3.30 \times 10^1$	$1.67 \times 10^{-4}$	$4.11 \times 10^{16}$
86	$1.69 \times 10^2$	$3.28 \times 10^{-5}$	$8.05 \times 10^{15}$
90	$8.62 \times 10^2$	$6.42 \times 10^{-6}$	$1.58 \times 10^{15}$
94	$4.40 \times 10^3$	$1.26 \times 10^{-6}$	$3.08 \times 10^{14}$
98	$2.25 \times 10^4$	$2.46 \times 10^{-7}$	$6.04 \times 10^{13}$
102	$1.15 \times 10^5$	$4.81 \times 10^{-8}$	$1.18 \times 10^{13}$

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