Pump-down model of vacuum chambers with adsorbing walls

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Abstract. The mathematical model is considered for the calculation of the pump-down characteristics of vacuum chambers with adsorbing walls. This model uses the dependence of the absorption heat on the logarithm of the coverage degree, which is obtained from the Freundlich adsorption isotherm. The dependences of pressure, gas release, adsorption heat and the amount of adsorbed gas on the pump-down time have been calculated. It is shown that there is a steady pump-down mode for water at 298 K, which does not depend on the chamber volume and the initial pressure, but is determined only by the area of the internal surface of the chamber.

1. Introduction
Vacuum chambers can contain a lot of gas adsorbed on their internal surfaces. The adsorbed gas is energetically connected to the surface and pumped down more slowly than the gas which is in the chamber volume. At high vacuum the pump-down time of the vacuum chamber is virtually completely determined by the time within which the adsorbed gases are pumped down [1–4]. It takes a lot of time to heat the vacuum chamber and remove the adsorbed gas, which reduces the productivity of vacuum plants. The adsorption of gases on the walls of vacuum chambers is largely dependent on the adsorption of water vapor when they are decompressed.

In literature there are two types of mathematical models which determine the amount of adsorbed gas on the internal surfaces of vacuum systems: a diffusion one [1] and an adsorption one [2]. The diffusion model implies that there are surface pores where gas is adsorbed, while the coefficient of gas diffusion in pores limits the rate at which it gets removed during pumping-down. The adsorption model considers a smooth surface, with the rate of gas removal being determined by condensation and evaporation processes.

This paper is dedicated to the development of the adsorption model. The paper [2] considers the capabilities for applying various adsorption equations in the adsorption pump-down model of vacuum systems and makes a conclusion about the viability of utilizing the Temkin isotherm for these purposes. The weak point of the Temkin equation is the assumption of the linear dependence of the adsorption heat on the coverage degree, which is not executed for water vapor adsorption on the walls of vacuum chambers. The experimental data on water adsorption on a stainless steel surface is well described by the Freundlich equation [3].

In our model we used the logarithmic dependence of adsorption heat on the coverage degree. The model makes it possible to calculate the dependences of pressure, the amount of absorbed gas, gas release, the adsorption heat on the pump-down time, and to determine the coefficients of the Freundlich adsorption isotherm by an inverse method from the pump-down curve.
2. Pump-down adsorption model of vacuum chambers

The mathematical pump-down model of vacuum chambers with adsorbing walls can be made if the processes of evaporation \( q_e \), condensation \( q_c \) and pump-down \( q_p \) are considered simultaneously (Figure 1).

The differential equation of mass transfer on the internal surfaces of vacuum chambers at the pump-down productivity \( q_p = 0 \) can be represented as:

\[
\frac{da}{dt} + \frac{a}{\tau_a(Q_a)} - K_p = 0,
\]

where \( a \) is the specific amount of adsorbed gas, m\(^3\)/Pa/m\(^2\); \( t \) is the time, s; \( p \) is the pressure, Pa;

\[
K = \frac{s \cdot N_A}{2.65 \cdot 10^{20} \sqrt{2\pi MRT} \sqrt{MT}} = \frac{s \cdot 1.08 \cdot 10^{4}}{2\pi} \sqrt{MT},
\]

\( s \) is the probability of condensation, \( \tau_a(Q_a) = \tau_0 \exp\left(\frac{Q_a}{RT}\right) \),

\( \tau_0 = 1.6 \cdot 10^{13} \cdot 298/T, R = 8.31 \cdot 10^3 J/kmol, N_A = 6.02 \cdot 10^{26} \) kmol\(^{-1}\).

![Figure 1. Conceptual pump-down model of vacuum chambers with adsorbing walls: 1 - vacuum chamber, 2 - vacuum pump.](image)

We use the linear dependence of absorption heat on the logarithm of the amount of adsorbed gas in the form [4]:

\[
Q_a = Q_1 - K_Q \lg(\theta),
\]

where

\[
Q_1 = RT \ln \left( \frac{1}{d m} \right) \quad K_Q = \frac{RT(1-m)}{0.43 \cdot m}.
\]

Here \( d \) and \( m \) are the coefficients of the Freundlich adsorption isotherm:

\[
a = dp^m,
\]

where \( a_m \) is the amount of gas in the monolayer per unit of the real surface, m\(^3\)/Pa/m\(^2\).

The equation (2) can be represented as:

\[
Q_a = E - K_Q \lg(\theta),
\]

where \( \theta \) is the coverage degree, \( \theta = a/a_m \), \( E \) is the condensation heat. For water on non-processed stainless steel at 298K, \( E = 4.4 \cdot 10^7 J/kmol, a_m = 0.116 \) m\(^3\)/Pa/m\(^2\), \( d = 0.0185, m = 0.34 \) [6]. At \( \tau_0 = 1.6 \cdot 10^{13} c, s = 0.4 \) and \( K = 59 \) it follows from (3) that \( Q_1 = 3.34 \cdot 10^3 J/kmol, K_Q = 1.12 \cdot 10^9 J/kmol \).

The differential equation of pumping down vacuum chambers with adsorbing walls at \( q_n = S p \):

\[
\frac{dp}{dt} + \frac{S \cdot p}{V} - \frac{da}{dt} \frac{F}{V} = 0,
\]

where \( V, F \) and \( S \) are the volume, the area of internal surface and effective pump-down rate of the vacuum chamber.
\[ S = K_u \cdot S_m (1 - \frac{p_m + p_a}{K_u p}), \]  

(7)

where \( S_m \) is the maximum pump-down rate, \( p_m \) is the ultimate pressure of the pump, \( K_u \) is the coefficient of the pump utilization (ratio of the effective and real pump-down rate of the pump), \( K_c \) is the coefficient of the pump compression, \( p_a \) is the outlet pressure.

Specific gas release \( q_a \) is determined as:

\[ q_a = \frac{da}{dt}. \]  

(8)

The mathematical pump-down model of vacuum chambers with absorbing walls can be represented by the following set of equations:

\[
\begin{align*}
\frac{da}{dt} + \frac{a}{\tau_a} - Kp &= 0, \\
\frac{dp}{dt} + \frac{p}{V/S} + \frac{da}{dt} \cdot \frac{F}{V} &= 0, \\
\tau_a &= 1.6 \times 10^{-13} \cdot \frac{298}{T} \exp\left(\frac{Q_a}{RT}\right), \\
Q_a &= E - K_Q \cdot \frac{\ln \left( \frac{a}{a_m} \right)}{\ln \left( \frac{a_{m_2}}{a_{m_1}} \right)}, \\
q_a &= \frac{da}{dt}, \\
S &= K_u \cdot S_m (1 - \frac{p_m + p_a}{K_u p}).
\end{align*}
\]  

(9)

The specific features of this model include utilizing: 1) the logarithmic dependence (5), which allows determining the value of absorption heat at any moment of the pump-down time; 2) the monomolecular coverage of the real rough surface; 3) the approximating function (7) for rapid pump-down of the chamber.

3. Calculations

The model (9) allows us to obtain a numerical solution, which determines the following, depending on the pump-down time: pressure, the amount of absorbed gas, the rate of adsorption gas release, adsorption heat and effective pump-down rate of the vacuum chamber. The parameters of the pump-down curve of water vapors (figures 2, 3) are calculated at \( T=298 \) K, \( v=V/S \), \( f=F/S \), \( p_m=10^8 \) Pa, \( p_v=10^0 \) Pa, \( K_e=10^{11} \), \( K_a=1 \), \( a_m=0.116 \) m³ Pa/m², \( E = 4.4 \times 10^7 \) J/kmol, \( K_Q = 1.12 \times 10^7 \) J/kmol.

Figure 2. The pump-down curves of water vapors at \( f=25\)s/m, \( p_f=10^1 \) Pa for various relative volumes of the chamber \( v \): 1 – 1 s, 2 – 100 s, 3 – 1000 s.

Figure 3. The pump-down curves of water vapors at \( f=25\)s/m, \( v=1s \) for various initial pressures \( p_1 \): 1 – \( 10^{-5} \) Pa; 2 – \( 10^{-3} \) Pa; 3 – \( 10^{-2} \) Pa, 4 – 1 Pa; 5 – 10 Pa.
The effect of the chamber volume on the pump-down curve (figure 2) is observed only in the initial phase. For \( V/F < 100 \) the duration of the initial phase does not exceed one hour.

The effect of the initial pressure on the pump-down curve in shown in figure 3. One hour after the pump-down starts, the curve is no longer dependent on the initial pressure.

4. Regular mode
When water vapors are pumped out at 298 K, the differential equation (1) in the model (9) can be substituted without noticeable loss of accuracy for the algebraic equation of the Freundlich adsorption isotherm (4). It means that the adsorption balance on the surface is achieved faster that the change of pressure occurs in the volume during pumping-down. The simplified model (9) after this substitution has an analytical solution. The pump-down time can be found from (4) and (6) after integrating \( dp/dt \) from \( t_1 \) to \( t \) and from \( p_1-p_m \) to \( p-p_m \):

\[
\Delta t = 2.3 \cdot v \cdot \lg \frac{p_1 - p_m}{p - p_m} + \frac{d \cdot m \cdot f}{1 - m} \left[ (p - p_m)^{m-1} - (p_1 - p_m)^{m-1} \right],
\]

where \( d \) and \( m \) are the coefficients of the Freundlich adsorption isotherm for water at 298 K, \( p_m \) is the ultimate pressure of the pump, Pa; \( p_1 \) is the initial pressure, Pa; \( v = V/S, f = F/S, s \cdot m^{-1} \); \( V \) is the chamber volume, \( m^3 \); \( F \) is the area of the chamber internal surface, \( m^2 \); \( S \) is the effective rate of chamber pump-down in \( m^3/s \) by approximation (7). The first summand in (10) determines the pump-down time of water vapors in the chamber volume, while the second one – on the internal surface.

The regular pump-down mode is understood as a mode when the pump-down process does not depend on the relative chamber volume, ultimate pressure of the pump and initial pump-down pressure.

The effect of the chamber volume on the pump-down curve in shown in figure 2. Meeting the condition:

\[
2.3 \cdot v \cdot \lg \frac{p_1 - p_m}{p - p_m} \ll \frac{d \cdot m \cdot f}{1 - m} \left[ (p - p_m)^{m-1} - (p_1 - p_m)^{m-1} \right]
\]

the pump-down curve stops depending on the chamber volume. In standard vacuum systems the effect of the working chamber volume on the pump-down curve usually becomes insignificant one hour after the pump-down process starts.

Under the condition

\[
(p_1 - p_m)/(p-p_m) > 10^2
\]

the pump-down curve does not depend on the initial pressure of the pump. At that \( \Delta t = t \).

Under the condition

\[
p >> p_m
\]

the pump-down curve does not depend on the ultimate pressure of the pump.

Under meeting the conditions (11-13) the regular mode settles and the equation (10) takes the form:

\[
p(t) = \left[ \frac{d m f}{3600 (1 - m) t} \right]^\frac{1}{1-m},
\]

where \( t \) is the pump-down time, h;

The pressure in the regular mode depends on the relative area of the internal surface of the chamber (Fig.4), and has the form of a straight line.

The dependence of the rate of water vapor adsorption gas release on the pump-down time according to the simplified model (9) is determined by the following expression:

\[
q_w(t) = \frac{da}{dt} = \frac{d m p^m}{v + f d m p^{m-1}}
\]

In the regular mode, when

\[
v << f d m p^{m-1}
\]
the relative volume \( v \) in the denominator (15) can be neglected. Then the rate of adsorption gas release becomes approximately equal to the productivity of the pump, while the specific rate of gas release

\[
q_a(t) = \frac{p(t)}{f}.
\]  

(18)

\[\text{Figure 4. The pump-down curves in the regular mode (14) at } d=0.0185: m = 0.34: 1 - f=1, 2 - f=25, 3 - f = 100.\]

The experimental data on the pressure in the regular pump-down mode can be represented as:

\[p(t) = A_t t^{-B},\]  

(19)

here \( t \) is the pump-down time, \( h \). From the comparison of (14) and (19) it follows

\[A_t = \left[ \frac{d m f}{3600(1-m)} \right]^{1-m}, \quad B = \frac{1}{1-m}.\]  

(20)

The coefficients of the Freundlich adsorption isotherm can be determined from the pump-down curves (19), using (20):

\[d = 3600(1-m)A_t^{1-m} m f \quad \text{and} \quad m = \frac{B -1}{B}.\]  

(21)

In the Freundlich adsorption isotherm \( m>0 \). In order to apply this model based on the Freundlich equation, as it follows from (21) condition \( B>1 \) has to be met.

5. Conclusion

The specifics of this model imply utilizing: the logarithmic dependence of adsorption heat on the degree of surface coverage; the mono-molecular coating of the real rough surface; the expanded approximating dependence of the effective rate of pumping the pressure down from the chamber. The model for water at 298 K has been used to calculate the dependences of pressure, gas release, adsorption heat and the amount of adsorbed gas on the pump-down time for a stainless steel vacuum chamber. It is shown that there is a regular pump-down mode, which does not depend on the chamber volume and the initial pressure, but is determined only by the area of the internal surface of the chamber. The coefficients of the Freundlich adsorption isotherm have been determined by inverse calculation from the pump-down curve.

References

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