ISSN 0915-633X

NATIONAL INSTITUTE FOR FUSION SCIENCE

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(Received - Sep. 17, 1997)

NIFS-515 Oct. 1997

RESEARCH REPORT
NIFS Series

NAGOYA, JAPAN

On the solution of the outgassing equation for the pump-down of an unbaked vacuum system

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Abstract

The outgassing equation based on the Temkin isotherm is presented to consider the outgassing behaviour in the pump-down of an unbaked vacuum system. A method to solve approximately the equation is discussed first and then solutions of outgassing rates are derived. Discussion is made how to derive appropriate solutions from the equation which are possible to predict the dependence of outgassing rate on pumping time and pumping speed. Solutions obtained finally are possible to explain consistently the outgassing behaviour observed experimentally for 304 stainless steel chamber after exposure to moist air concerning the dependence of outgassing rate on time and pumping speed.

Key words: outgassing rate, Temkin isotherm, coverage, heat of adsorption, mean residence time, sticking probability, pumping parameter.

1. Introduction

Recently, I and my colleagues [1] measured the outgassing rate of an unbaked stainless steel chamber after exposure to moist air using pumping orifices of various sizes in the pumping speed range 0.35 l/s - 182 l/s, and found that the measured outgassing rate q obeys a power law $q = \text{const.} t^{-\phi}(S/A)^m$ where t is the pumping time, S/A is the pumping parameter defined as the ratio of pumping speed S to the surface area A of chamber, and exponents of ϕ , m are given as $|\phi - 1| \geq 0$ (i.e. ϕ is about 1) and $0 < m \leq 1$. The time dependence of outgassing rate can be explained with the pumping-down models [2,3] based on the Temkin isotherm and the extended Temkin isotherm but the dependence of outgassing rate on pumping speed cannot be explained by such pumping-down models. Then, in order to explain theoretically the experimental result on the dependence for pumping speed, an outgassing model to describe the outgassing rate of a vacuum system in a reversible-adsorbed phase was constructed and an outgassing equation was derived. The detailed derivation procedure of the outgassing equation has been reported elsewhere [4].

In this paper, it is discussed how to solve the outgassing equation and how to extract fine outgassing behaviour from the obtained solution.

2. Outgassing equation

In order to consider the change of outgassing rate with time during the pump-down of an unbaked vacuum system, we have first assumed that the initial surface coverage in the pump-down changes by less than one monolayer and adsorption is fully reversible. Then we have derived the outgassing equation for the vacuum system by considering mass conservation of equations for the total number of gas molecules in the system and the number of adsorbed gas molecules on the wall surface of the vacuum system as follows [1,4]:

$$q = \sigma_m \left(-\frac{d\theta}{dt} \right) \qquad (1)$$

and

$$-\frac{d\theta}{dt}=\frac{a}{A}\frac{1}{s+\frac{a}{A}}\frac{\theta}{\tau}, \quad (2)$$

where q is the outgassing rate, θ is the surface coverage defined as fraction of occupied sites with adsorbed molecules on a solid surface, σ_m is the number of adsorbed molecules per unit area in monolayer coverage, a/A is the pumping parameter, s is the effective sticking probability and τ is the mean residence time. Eq.(2) describes the outgassing rate at a quasi-steady state when the pressure of the vacuum system changes very slowly with pumping time. In addition the parameters s, τ and a/A in Eq.(2) are defined as

$$s = s_0(1-\theta), \quad (3)$$

$$\tau = \tau_0 \exp\left(\frac{E}{RT}\right), \quad (4)$$

and

$$a\left(\frac{v}{4}\right) = S, \quad (5)$$

where s_0 is the sticking probability on empty sites, τ_0 is the nominal period of vibration of an adsorbed molecule on a solid surface, E is the heat of adsorption, R is the gas constant ,T is the absolute temperature, a is the equivalent surface area for pumping speed of S, v is the average velocity of gas molecule in gas phase and A is the surface area of the wall surface. Here if we consider the Temkin isotherm in which the heat fall of E is linear with increasing θ, E in Eq.(4) may be expressed as

$$E = E_c + \Delta E(1-\theta), \quad (6a)$$

$$\Delta E = E_m - E_c, \quad (6b)$$

where ΔE is the magnitude of variation of heat of adsorption, E_c is the minimum heat of adsorption at θ = 1 and E_m is the maximum heat of adsorption at θ = 0. Using Eqs.(6a,b), Eq.(4) is expressed as

$$\tau = \tau_c \exp[b(1-\theta)], \quad (7a)$$

where

$$\tau_c = \tau_0 \exp\left(\frac{E_c}{RT}\right), \quad (7b)$$

and

$$b = \frac{\Delta E}{RT}. \quad (7c)$$

By substituting Eqs.(3) and (7a) into Eq.(2), we have the following form of variable separation:

$$F(\theta)\left(-\frac{d\theta}{dt}\right) = \frac{\gamma}{\tau_c \exp(b)}, \quad (8a)$$

where

$$F(\theta) = \exp(-b\theta)\left(\frac{1-\theta+\gamma}{\theta}\right), \quad (8b)$$

and

$$\gamma = \frac{a}{As_0}. \quad (8c)$$

What we can have such a form of variable separation as Eq.(8a) for Eq.(2) means that the differential equation for coverage is mathematically solved. However, we must depend on numerical analysis for obtaining a solution, because the integration of left-hand side of Eq.(8a) is analytically difficult.

3. Approximation method to solve the outgassing equation

3.1 Approximate expression of F(θ)

Here we try to solve Eq.(8a) by approximating F(θ) with a simple function so that we can integrate F(θ) analytically. Since the main term in F(θ) is exp(-bθ)/θ, if we express it by letting x=bθ as $\exp(-b\theta)/\theta = b\exp(-x)/x \equiv G$, the total differential of $\ln G$ is given by

$$dG/G = -dx - dx/x.$$

From this relation we can say that if $1 < x$ (i.e. $1/b < \theta$), the change of G with x is dominated by the function exp(-x) and if $x < 1$(i.e. $\theta < 1/b$), it is in turn dominated by the function 1/x. Thus we may express approximately the function $F(\theta)$ with an exponential function or a fractional function according to the range of coverage. Before determining approximated functions, we here assume reasonable numerical values for the specific parameters of b and γ as follows: b=20 (i.e. ΔE =12 kcal/mol for E_m=23 kcal/mol and E_c = 11kcal/mol) and γ is variable between 10^{-5} to 10 for s_0=0.1 Then, using two constants of k and f we may express $F(\theta)$ with the following exponential function for the range of $1/b(=0.05) \leq \theta \leq 1$,

$$F(\theta) = f\exp\left(-\frac{\theta}{k}\right). \qquad (9)$$

We can determine the average value of constant 1/k by comparing derivatives $dF(\theta)/d\theta$ between Eqs.(8b) and (9) as

$$\overline{\frac{1}{k}} = \int_1^{\frac{1}{b}}\left[b+\frac{1}{\theta}+\frac{1}{1+\gamma-\theta}\right]d\theta/\int_1^{\frac{1}{b}}d\theta \qquad (10a)$$

and using Eq.(10a) the average value of f is given as

$$\overline{f} = \int_1^{\frac{1}{b}}\left[\exp\left(\frac{1}{k}-b\right)\theta\right]\left(\frac{1-\theta+\gamma}{\theta}\right)d\theta/\int_1^{\frac{1}{b}}d\theta. \qquad (10b)$$

(1) Approximation with power function for the range of $0.8 \leq \theta \leq 1$

In the calculation of the average value of 1/k by Eq.(10a), we face a peaking that the integration of $1/(1+\gamma-\theta)$ gives extreamely a large number for small γ at θ=1. However, we can avoid the peaking, since it is possible within the error of 10% to replace the term $(1-\theta)$ with $\ln(1/\theta)$ in Eq.(6a) for the range of $0.8 \leq \theta \leq 1$. Then the mean residence time for $E = E_c + \Delta E \ln(1/\theta)$ is rewritten as

$$\tau = \tau_c \theta^{-b} . \qquad (11)$$

By combining Eqs.(2),(8a) and (11), we have

$$F(\theta) = \theta^{-(b+1)}[(1+\gamma)-\theta], \quad \text{for} \quad 0.8 \le \theta \le 1 . \quad (12)$$

(2) Constants k , f for the middle range of $0.2 \le \theta \le 0.8$

Since the range of high coverage near 1 is treated separately, we here try to estimate the constants 1/k and f using Eqs.(10a) and (10b) for the remaining range of $1/b(=0.05) \le \theta \le 0.8$. An interest is to estimate the values of 1/k and f when the change of coverage remains in the middle range of coverage near $\theta = 1/2$, which is the assumption in the Temkin isotherm that $\theta \to 1/2$ so that $\theta/(1-\theta) \to 1$. We may expect such situation for the pumpdown of the chamber by small pumping speed. If we can apply the assumption of $\theta/(1-\theta) \approx 1$ for the middle range, Eq.(8b) is expressed as

$$F(\theta) = \exp(-b\theta)\left(1+\frac{\gamma}{\theta}\right). \qquad (13)$$

Then we can estimate average values of 1/k and f for $0.2 \le \theta \le 0.8$ and $10^{-4} \le \gamma \le 10$ using Eqs. (9) and (13). The results are shown in Table 1.

(3) Constants k , f for the range of $0.2 \le \theta \le 0.8$ and $1/b(=0.05) \le \theta \le 0.8$

Table-2 shows average values of 1/k and f calculated using Eqs.(8b) and (9) for $0.2 \le \theta \le 0.8$ and $10^{-4} \le \gamma \le 10$. Table-3 shows the average values of constants when the lower Integral limit of θ is extended further from θ=0.2 to θ=1/b=0.05.

(4) Approximation with a fractional function for the range of $0 \le \theta \le 1/b \ (= 0.05)$

When the coverage becomes less than 1/b, we can put that $\exp(-b\theta)$ in the function F(θ) is nearly equal to 1. Then Eq.(8b) is expressed as

$$F(\theta) = \frac{1+\gamma}{\theta} . \qquad (14)$$

3.2 Approximate solution of $\theta(t)$

We try to derive solution of $\theta(t)$ as a function of time from Eq.(8a) using the approximated forms for $F(\theta)$.

(1) For $0.8 \le \theta \le 1$,by combining Eqs.(8a),(11) and (12) we have

$$\theta^{-(b-1)}\left[(1+\gamma)-\theta\right]\left(-\frac{d\theta}{dt}\right)=\frac{\gamma}{\tau_c} \quad . \qquad (15)$$

The integration of

$$-\int_1^\theta \left[(1+\gamma)-\theta\right]\theta^{-(b+1)}d\theta=\left(\frac{\gamma}{\tau_c}\right)\int_0^t dt ,$$

gives for the approximation of $b-1 \cong b$ the following relation:

$$\left[(1+\gamma)-\theta\right]\theta^{-b}=\frac{b\gamma}{\tau_c}\left(t+\frac{\tau_c}{b}\right) . \quad (16)$$

By substituting again Eq.(16) into Eq.(15) the integration gives

$$\theta(t)=\left[\frac{t_0}{t+t_0}\right]^{\frac{1}{b}} \qquad \text{for} \quad t_0=\frac{\tau_c}{b} . \quad (17)$$

(2) For $0.2 \le \theta \le 0.8$, from Table-1 if γ is less than 10^{-2}, we can set that kb=1 and f=0.6. Then by letting

$$F(\theta)=f\exp(-b\theta) , \qquad (18)$$

the integration of Eq.(8a),

$$-\int_{\theta_0}^{\theta}\exp(-b\theta)d\theta=\frac{\gamma}{f\tau_c\exp(b)}\int_0^t dt ,$$

gives

$$\theta(t) = -\frac{1}{b}\ln\left[\frac{b\gamma}{f\tau_c \exp(b)} \cdot t + \exp(-b\theta_0)\right], \quad (19)$$

where $\theta_0(=0.8)$ is the initial coverage at t=0.

(3) For $0.2 \le \theta \le 0.8$, from Table-2 we can set that kb <1 and f = 3 ~ 32 . Then using Eq.(9), the integration of Eq.(8a) is given as

$$-\int_{\theta_0}^{\theta} \exp\left(-\frac{\theta}{k}\right) d\theta = \frac{\gamma}{f\tau_c \exp(b)} \int_0^t dt \ , \ (20)$$

and it gives

$$\theta(t) = -k \ln\left[\frac{\gamma}{fk\tau_c \exp(b)} \cdot t + \exp\left(-\frac{\theta_0}{k}\right)\right]. \quad (21)$$

(4) For $0 \le \theta \le 1/b \ (= 0.05)$,by substituting Eq.(13) into Eq.(8a) we have the integration of

$$-\int_{\theta_0}^{\theta} \frac{d\theta}{\theta} = \frac{\gamma}{1+\gamma} \cdot \frac{1}{\tau_c \exp(b)} \int_0^t dt, \quad (22)$$

and it gives

$$\theta(t) = \theta_0 \exp\left[-\frac{\gamma}{1+\gamma} \cdot \frac{t}{\tau_c \exp(b)}\right]. \quad (23)$$

4. Outgassing rate as time derivative of θ(t)

Now we can express the outgassing rate q(t) using the solution θ(t) derived in Section 3.2. As defined in Eq.(1), it is given by differentiating θ(t) as follows:

(1) for $0.8 \le \theta \le 1$,

$$q(t) = \frac{\sigma_m}{\tau_c}\left[\frac{t_0}{t+t_0}\right]^{1+\frac{1}{b}}, \qquad \text{for } t_0 = \frac{\tau_c}{b}, \ (24a)$$

(2) for $0.2 \le \theta \le 0.8$ and kb = 1,

$$q(t) = \frac{\sigma_m}{b(t+t_0)}, \quad \text{for } t_0 = \frac{f\tau_c}{b\gamma}\exp[b(1-\theta_0)], \quad (24b)$$

(3) for $0.2 \le \theta \le 0.8$ and kb < 1,

$$q(t) = \frac{k\sigma_m}{(t+t_0)}, \quad \text{for } t_0 = \frac{kf\tau_c}{\gamma}\exp\left(b - \frac{\theta_0}{k}\right), \quad (24c)$$

(4) for $0 \le \theta \le 1/b\ (= 0.05)$,

$$q(t) = \frac{\gamma}{1+\gamma} \cdot \frac{\sigma_m\theta_0}{\tau_c \exp(b)} \exp\left[-\frac{\gamma}{1+\gamma} \cdot \frac{t}{\tau_c \exp(b)}\right]. \quad (24d)$$

Eq.(24a) shows that the outgassing rate obeys the power law $q(t) = \text{const.}t^{-\phi}$ where ϕ is slightly greater than 1. This time dependence is acceptable, since we can express the variation of heat of adsorption in the Temkin isotherm in the range of high coverage near θ=1 with that in the Freundlich isotherm under the approximation of $(1-\theta) \cong \ln(1/\theta)$. The outgassing rate is not dependent on the pumping speed, since no pumping parameter appears in the expression of q(t). Eqs.(24b) and (24c) show that the outgassing rate obeys the power law $q(t) = \text{const.}t^{-\phi}$ where ϕ is just equal to 1 and the outgassing rate is not dependent on pumping speed, since pumping parameter does not appear explicitly in the expression of q(t) except that the constant k in Eq.(24c) has weak dependence on γ. The constant t_0 which appears in Eqs.(24a),(24b) and (24c) can be explained as delay time or transit time until the outgassing rate builds up from 0 to a steady state value when the pump-down of vacuum system is started. This time becomes longer when the pump-down is started at a smaller initial coverage and with a smaller pumping parameter. Eq.(24d) shows that the outgassing rate decreases exponentially with pumping time and depends on the pumping speed, because the curvature of q is expressed by $\gamma/(1+\gamma)$.

5. Outgassing rate of higher order approximation

According to recent results [1,5,6] of outgassing measurements for 304 stainless steel chambers after exposure to moist air, it has been suggested that the outgassing rate obeys a power law $q(t) = \text{const.}t^{-\phi}$ where ϕ varies from 0.83 to 1.3. For such experimental results, it is possible to explain only the power law $q(t) = \text{const.}t^{-\phi}$ where $1 < \phi$ and $\phi = 1$ using the results of Eqs.(24a),(24b) and (24c) but is difficult to explain the power law of $\phi < 1$. The reason why the power law of $\phi < 1$ cannot be explained theoretically should be asked for that we express the outgassing rate by differentiating the solution $\theta(t)$. We can have another expression for the outgassing rate by substituting directly the solution $\theta(t)$ into Eq.(2). Since the time dependent term in Eq.(2) is mainly represented with $\theta/\tau(\theta)$, for example it is shown for the solution Eq.(21) as

$$q(t) \propto \frac{k\sigma_m}{\tau_c \exp\left[b(1-\theta_0)\right]}\left[\frac{t_0}{t+t_0}\right]^{kb} \ln\left[\frac{kf\exp(b)}{\gamma}\left(\frac{1}{t+t_0}\right)\right].$$

We can see from this expression that the outgassing rate vs. time curve has the behaviour of $q(t) = \text{const.}t^{-\phi}$ where $\phi = kb < 1$. Then let us consider how a consistent expression of outgassing rate with experimental results should be derived from Eq.(2), when the approximated solution of $\theta(t)$ is given by Eq.(19) or Eq.(21). If we derive a second order differential equation for coverage from Eq.(2), it is expressed by combining with Eq.(1) as follows:

$$\frac{1}{q}\frac{dq}{dt} = -\left[\frac{1}{\tau}\frac{d\tau}{dt} + \frac{1}{s+\frac{a}{A}}\frac{ds}{dt} - \frac{1}{\theta}\frac{d\theta}{dt}\right], \quad (25a)$$

and since the third term of the right-hand side can be rewritten again using Eq.(2) as $[(a/A)/(s+a/A)]/\tau$, we at last have

$$\frac{1}{q}\frac{dq}{dt} = -\left[\frac{1}{\tau}\frac{d\tau}{dt} + \frac{1}{s+\frac{a}{A}}\frac{ds}{dt} + \frac{a}{A}\frac{1}{s+\frac{a}{A}}\frac{1}{\tau}\right]. \quad (25b)$$

The right-hand side of Eq.(25b) shows that q is described with three terms. In particular the third term as a total differential of θ appears due to the pump-down of the vacuum system (i.e. $a/A \neq 0$). The integration of Eq.(25b) for the integration limits from t=0 to t is given by

$$\frac{q(t)}{q(0)}=\frac{\tau(0)}{\tau(t)}\left[\frac{s(0)+\frac{a}{A}}{s(t)+\frac{a}{A}}\right]\exp\left[-\frac{a}{A}\int_0^t\frac{dt}{\tau\left(s+\frac{a}{A}\right)}\right]. \quad (26)$$

In order to obtain the expression of outgassing rate from Eq.(26), it is necessary to calculate the time integration of the exponential term. Using Eq.(21), we can transform $s(\theta)$ and $\tau(\theta)$ to time functions respectively as

$$\tau(\theta)=\tau_c\exp[b(1-\theta)]=\tau_c\exp(b)[\beta(t+t_0)]^{kb}\equiv\tau(t)\,. \quad (27a)$$

and

$$s(\theta)=s_0(1-\theta)=s_0+s_0k\ln[\beta(t+t_0)]\equiv s(t)\,, \quad (27b)$$

where

$$\beta=\frac{\gamma}{kf\tau_c\exp(b)}\,, \quad (27c)$$

and

$$\beta t_0=\exp\left(-\frac{\theta_0}{k}\right). \quad (27d)$$

Then, using Eqs.(27a) and (27b) the integration is expressed as

$$I=-\left(\frac{a}{A}\right)\int_0^t dt\frac{1}{s_0k[\ln\beta(t+t_0)+\lambda]}\frac{1}{\tau_c\exp(b)}\left[\frac{1}{\beta(t+t_0)}\right]^{kb}\,, \quad (28a)$$

where

$$\lambda = \frac{1+\gamma}{k} . \qquad (28b)$$

By letting $x = \beta(t + t_0)$ and $u = x\exp(\lambda)$, I is expressed as

$$I = -f \cdot \exp[-\lambda(1-kb)] \int_{u_0}^{u} \frac{du}{u^{kb} \ln u}, \qquad (29a)$$

and we have for kb=1

$$I = \ln\left[\frac{s(0)+\dfrac{a}{A}}{s(t)+\dfrac{a}{A}}\right]^{f}, \qquad (29b)$$

and for kb < 1, since the integral of Eq.(29a) becomes logintegral which is expressed as

$$\int \frac{du}{u^{kb}\ln u} = \mathrm{li}\left(u^{1-kb}\right) = 0.57721 + \ln\left|\ln u^{(1-kb)}\right| + \sum_{r=1}^{\infty} \frac{[(1-kb)\ln u]^{r}}{r \bullet r!},$$

where the number 0.57721 is Euler's constant. Then we have

$$I = \ln\left[\frac{1-\theta_0+\gamma}{1-\theta+\gamma}\right]^{\alpha}\left[\frac{t_0}{t+t_0}\right]^{\alpha\eta(1-kb)}, \qquad (29c)$$

where

$$\alpha = f \cdot \exp[-\lambda(1-kb)] = f\exp\left[-(1+\gamma)\left(\frac{1}{k}-b\right)\right], \qquad (29d)$$

and

$$\eta = \frac{\sum_{r=1}^{\infty} \dfrac{[(1-kb)\ln u]^{r}}{r \bullet r!}}{(1-kb)\ln u} . \qquad (29e)$$

Thus Eq.(26) gives the following expressions for q(t) :

(1) for kb=1 by combining Eqs(26) and (29b)

$$q(t)=\frac{\sigma_m}{\tau_c}\left[\frac{t_0}{t+t_0}\right]\left[\frac{1-\theta_0+\gamma}{1-\theta+\gamma}\right]^{1+f}, \qquad (30a)$$

(2) for kb<1 by combining Eqs(26) and (29c)

$$q(t)=\frac{\sigma_m}{\tau_c}\left[\frac{t_0}{t+t_0}\right]^{kb+\alpha(1-kb)}\left[\frac{1-\theta_0+\gamma}{1-\theta+\gamma}\right]^{1+\alpha} . \qquad (30b)$$

Now if we approximate in Eq.(30a) that $s(0)=s_0(1-\theta_0)\approx 0$ for $\theta_0\cong 1$ at t=0 and $s(t)=s_0[1-\theta(t)]\cong s_0$ for $\theta(t)\approx 0$ after long pump-down, the last brackets term of the right-hand side is expressed as

$$\left[\frac{1-\theta_0+\gamma}{1-\theta+\gamma}\right]=\frac{\gamma}{1+\gamma} ,$$

and the time ratio t_0/τ_c is replaced as

$$\frac{t_0}{\tau_c}=\frac{f}{b\gamma}\exp[b(1-\theta_0)],$$

then Eq.(30a) is given as

$$q(t)=\sigma_m \exp[b(1-\theta_0)]\frac{\gamma^f}{b(t+t_0)}\left[\frac{1}{1+\gamma}\right]^{1+f} . \qquad (32)$$

Similarly we can simplify Eq.(30b). Let us first examine the magnitude of parameters α and η. By using parameter values of k and f as a function of γ shown in Table 1 and 2, we can calculate α and η with Eq.(29d). The following conditions are used for the calculation of u_0 and u:

$\theta(0)=\theta_0=0.8$ at $t=0$ and $\theta(t)=0.2$ at $t=t$ for Table 1 and Table 2 .

The calculated values of α and η for variation of γ are shown in Tables 4 and 5. For the condition of kb < 1, as shown in Tables 4 and 5, α is regarded to be very small number compared with 1. Then we can treat the last brackets term of the right-hand side in Eq.(30b) as

$$\left[\frac{1-\theta_0+\gamma}{1-\theta+\gamma}\right]^{1+\alpha} \cong \frac{\gamma}{1+\gamma} \quad ,$$

and further we may regard the coefficient η as a constant value for the variation of γ. In addition the term t_0/τ_c is expressed using Eqs.(27c) and (27d) by letting ϕ = kb+$\alpha\eta$(1-kb) as

$$\frac{t_0^{\phi}}{\tau_c} = \left(\frac{1}{\tau_c}\right)^{1-\phi}\left[\frac{f}{\gamma}\exp\left(-\frac{\theta_0}{k}+b\right)\right]^{\phi} k^{\phi}$$

and by putting that $\theta = \theta_0 \cong 1$ in the equality between Eqs.(8b) and (9), since the expression can be rewritten as

$$\exp\left(-\frac{\theta_0}{k}+b\right) = \frac{\gamma}{f},$$

then we have the following relation :

$$\frac{t_0^{\phi}}{\tau_c} \cong \left(\frac{1}{\tau_c}\right)^{1-\phi} k^{\phi}.$$

Thus we have the simplified expression of Eq.(30b) as

$$q(t) \cong \sigma_m\left(\frac{1}{\tau_c}\right)^{1-\phi}\left(\frac{k}{t+t_0}\right)^{\phi}\left(\frac{\gamma}{1+\gamma}\right), \quad \phi = \mathrm{kb} + \alpha\eta(1-\mathrm{kb}). \qquad (33)$$

Eq.(32) shows that the outgassing rate in the middle range of coverage is proportional to $\gamma^f t^{-1}$ where f=0.6 <1 and kb=1. Eq.(33) shows that the outgassing rate in the middle range of coverage is proportional to

$[\gamma/(1+\gamma)]t^{-\phi}$ where $\phi < 1$.

6. Discussion and summary

(1) Solution of outgassing equation

In order to solve analytically the outgassing equation of Eq.(2), it is essential to find out reasonable approximated expressions for the function $F(\theta)$ which is given as the product of two functions, $\exp(-b\theta)$ and $(1-\theta+\gamma)/\theta$. By taking into account that the dominant contribution of each function to the change of $F(\theta)$ with decrease of θ appears separately in different ranges of coverage, $F(\theta)$ can be approximated with an exponential function or a fractional function. However, only for the high coverage range near $\theta = 1$, $F(\theta)$ should be rather replaced from the exponential function to a power function to avoid the peaking of constant k at $\theta=1$. Using three expressions for $F(\theta)$, the solutions $\theta(t)$ of Eq.(2) can be derived. Then, the outgassing rates can be also determined with the solution $\theta(t)$.

(2) Expression of outgassing rate

There are two methods to express the outgassing rate q(t) with the solution $\theta(t)$. One is to express q(t) using Eq.(1) by differentiating directly $\theta(t)$. The other is to express q(t) by substituting $\theta(t)$ into the right-hand side of Eq.(2). In either way, same expressions for outgassing rate are drawn for the high range of $0.8 \le \theta \le 1$ and the low range of $0 \le \theta \le 1/b$, but only for the middle range of $1/b \le \theta \le 0.8$ the expression of outgassing rate differs with the approach. Although Eqs.(24a),(24b) and(24c) are derived by the differential method, these predict the obedience of outgassing rate to the power law $q(t) \propto t^{-\phi}$. In particular, in the comparison with the experimental results[1,5,6] on the power law dependence of outgassing rate, Eq.(24a) predicts the power law that the exponent ϕ becomes slightly greater than 1, and Eqs.(24b) and (24c) predict the power law that ϕ becomes just 1. However, the power law that ϕ becomes smaller than 1 can not be explained by any of the above expressions. On the other hand, when the outgassing rate is expressed by the substitution of $\theta(t)$ into Eq.(2), since the outgassing rate is characterized mainly with the reciprocal of mean residence time, the time dependence of outgassing rate is described as $1/\tau(\theta) = 1/\tau(t) \propto t^{-\phi}$ where ϕ =kb. As shown in

Table 1 and 2, the constant k is variable depending on the value of γ and the value of lower limit of θ which is permissible for the middle range. If the lower limit value is θ =0.2, kb is nearly equal to 1 (i.e. kb=1) for $\gamma < 0.1$ but becomes slightly less than 1 (i.e. kb < 1) for $\gamma > 0.1$. Thus, in order to explain theoretically the power law of $\phi < 1$ for outgassing rate observed experimentally, the term $\tau(\theta)$ must appear explicitly in the expression of outgassing rate q(t). From this reason a more accurate expression for outgassing rate should be derived from Eq.(2). In the meaning that the differential method for $\theta(t)$ does not show the exponent value smaller than 1, one can regard that Eqs.(19) and (21) are solutions of zero order approximation for the outgassing equation. In addition, as seen in Table 2, when coverage θ becomes smaller than $\theta=1/2$, kb becomes less than 1 (i.e. kb < 1) for almost all γ values. Such situation as that the lower limit of coverage shifts to a very small value, may be expected practically in the pump-down of a vacuum system after mild baking or discharge cleaning for the vacuum system. In Tables 1 and 2, it is noticed that the maximum limit of γ is 10, since γ =10 is equivalent to a/A =1 for the assumed value of s_0 = 0.1. Thus the variable range of γ for the pump-down of usual vacuum system may be considered to be as $\gamma < 10$.

(3) Outgassing rate of higher order approximation

It is very important to discuss the outgassing behaviour in the middle range of coverage, since the coverage of adsorbed molecules on the wall of a vacuum chamber in a reversible-adsorbed phase will almost remain in the middle range. The outgassing rate in this range can be derived by solving Eq.(25b). To solve it results in calculating the solution of higher order approximation for coverage, which appears as the time integral of the exponent in Eq.(26). However, since it is difficult to integrate analytically the exponent, numerical treatment is necessary. So that parameters of α and η are introduced to evaluate the integration for the case of kb < 1 and are calculated for various γ value. As a result of the numerical evaluation as shown in Tables 4 and 5, the following conclusions are drawn:

(i) when $F(\theta)$ is expressed by Eq.(13) in the middle range of $0.2 \le \theta \le 0.8$, the outgassing rate obeys the power law $q(t) = \mathrm{const.} t^{-\phi} \gamma^{f}$ where ϕ=kb=1 and f=0.6

for $\gamma \le 0.1$, and ϕ <1 and γ^f changes to $[\gamma/(1+\gamma)]$ for $\gamma > 0.1$,
(ii) when F(θ) is expressed by Eq.(8b) in the middle range of $0.2 \le \theta \le 0.8$, the outgassing rate obeys the power law $q(t) = \text{const}.t^{-\phi}[\gamma/(1+\gamma)]$ where $\phi<1$. There have been proposed for some pumping-down models[2,3] for a vacuum system in a reversible-adsorbed phase based on the Temkin isotherm. These models suggest that the outgassing rate obeys the power law t^{-1} and not depends on pumping speed. This suggestion differs from the results of this outgassing model. The difference occurs probably by the reason that as discussed above, since only solution of zero order approximation for coverage is derived in the pumping-down models, as a result such a power law of $\phi < 1$ cannot be drawn. Redhead[3] has shown numerically using the pumping-down model based on the extended Temkin isotherm that the exponent ϕ of $t^{-\phi}$ behaviour in the pressure vs. time curve is able to become less than 1, if the minimum heat of adsorption starts to increase from an initial value with decrease of coverage. However, in this study it may be rather explained as a result that the function F(θ) changes from the exponential function to the fractional function with decrease of θ, i.e. the value of 1/k starts to increase rapidly for coverage below θ=1/2. In addition, it may be an important prediction of the outgassing model that the outgassing rate in a reversible-adsorbed phase is dependent on pumping speed, since any pumping-down model has not so far remarked on such dependence.

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Table captions

Table 1 : Constants 1/k and f calculated for the approximation $[1+(\gamma/\theta)]e^{-b\theta} = fe^{-\theta/k}$ in the ranges of $0.2 \le \theta \le 0.8$ and $10^{-4} \le \gamma \le 10$.

Table 2 : Constants 1/k and f calculated for the approximation $(1+\gamma-\theta)e^{-b\theta}/\theta = fe^{-\theta/k}$ in the ranges of $0.2 \le \theta \le 0.8$ and $10^{-4} \le \gamma \le 10$.

Table 3 : Constants 1/k and f calculated for the approximation $(1+\gamma-\theta)e^{-b\theta}/\theta = fe^{-\theta/k}$ in the ranges of $0.05 \le \theta \le 0.8$ and $10^{-5} \le \gamma \le 10$.

Table 4 : Constants α and η_θ calculated using parameter values of k, f and γ given in Table-1 for the condition of kb<1.

Table 5 : Constants α and η_θ calculated using parameter values of k, f and γ given in Table-2.

Table-1

γ	10	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}
$\frac{1}{k}-b$	1.33	0.98	0.29	0.04	0	0
$\frac{1}{k}$	21.33	20.98	20.29	20.04	20.0	20.0
kb	0.937	0.953	0.985	~ 1	1	1
f	26.0	3.17	0.85	0.62	0.60	0.60

Table-2

γ	10	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}
$\frac{1}{k}-b$	1.78	2.24	2.93	3.19	3.22	3.67
$\frac{1}{k}$	21.78	22.24	22.93	23.19	23.22	23.67
kb	0.918	0.899	0.872	0.862	0.861	0.845
f	31.6	5.91	3.24	3.08	3.07	3.79

Table-3

γ	10	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
$\frac{1}{k}$	22.84	23.26	24.03	24.29	24.33	24.33	24.33
f	77.0	12.96	7.65	7.16	7.21	7.22	7.22

Table-4

γ	10	1	0.1
α	$1.1735x10^{-5}$	0.4465	0.6178
$\eta_{0.8}$	$4.6072x10^{3}$	1.3705	1.0217
$\eta_{0.2}$	$9.0779x10^{3}$	1.6870	1.0691

Table-5

γ	10	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}
α	$9.912x10^{-8}$	$6.6980x10^{-2}$	$1.2907x10^{1}$	$1.2283x10^{-1}$	$1.2227x10^{-1}$	$9.6301x10^{-2}$
$\eta_{0.8}$	$2.476x10^{5}$	2.3883	1.2709	1.1959	1.1882	1.2181
$\eta_{0.2}$	$6.396x10^{5}$	4.4894	2.359	2.3092	2.3048	2.6771

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