

Average diffusion-to-the-wall times for laser-tagged molecules in a long cylinder

J.W. Eerkens

CRISLA Laboratory, Nuclear Engineering, University of Missouri, Columbia, MO 65211, USA
(Fax: +1-573/884-4801, E-mail: eerkenj@missouri.edu)

Received: 5 June 2000/Revised version: 31 January 2001/Published online: 27 April 2001 – © Springer-Verlag 2001

Abstract. An approximate closed-form expression is derived for the average wall-reaching rate k_W or time $\tau_W = k_W^{-1}$ of laser-tagged molecules diluted in an inert carrier gas migrating to the wall of a long cylinder where they are removed with sticking coefficient η_W . The exact equation for the sticky wall problem requires a trial-and-error solution of a transcendental relation with Bessel-functions. With the aid of the Fermi–Amaldi albedo theory, an explicit “compromise” relation is derived which approximates the exact diffusion curve of k_W versus η_W rather well. The result is applied to obtain curves of k_W versus η_W at different gas mix pressures for UF_6 diluted in N_2 .

PACS: 02; 34; 68.45

In many laser-induced reaction and condensation changing processes, one needs to know the average rate k_W or travel time $\tau_W = k_W^{-1}$ at which newly laser-created molecular species A in a gas, migrate to and are captured on the wall inside a long tube. The molecules A are assumed to be dispersed through an inert gas (e.g. A = SF_6 in He) and may be laser-excited (e.g. A = SF_6^*) by a laser beam that passes through a cylindrical irradiation cell containing the gas mixture; or the molecules A may be new non-volatile reaction products from a laser-induced gas-phase reaction; or A may represent a molecule such as QF_6 which is mixed in with a carrier gas B (e.g. He, N_2 , Ar, Xe, etc.) that is suddenly injected into and passed through a (cooled) tube, whose wall can react with QF_6 or is at a low temperature on which QF_6 can condense out. After admission into the tube, the $\text{QF}_6^{(*)}$ diffuses to the tube walls where it is absorbed, condensed, de-excited or undergoes a chemical surface reaction.

At the wall, it is assumed that some molecules A are scattered back into the gas and some are captured or annihilated due to adsorption, condensation, deexcitation or a wall-catalyzed chemical reaction. We shall assume that a fraction η_W of all molecules A striking the wall will be annihilated or retained by it, and $1 - \eta_W$ are bounced back into the gas.

This problem has been analyzed before [1], but its solution requires trial and error steps of a transcendental equation with Bessel functions. In this paper we derive a convenient closed-form solution based partly on Fermi–Amaldi’s albedo theory and partly on an analytic approximation.

If $\eta_W \neq 0$, the molecular concentration $N_A(r, t)$ of A (cm^{-3}) must drop with time and a time-varying radial profile $N_A(r, t)$ will be set up with the highest value $N_A(r = 0) = N_c$ at the center of the tube. To find the average migration time, we study the fate of an imaginary tagged group of molecules A created at instant $t = 0$ in a time interval $\delta(t)$, even though the production of A may be continuous. The initial concentration of molecules A at $t = 0$ will be assumed to be either a line source (at $r = 0$), or be uniformly distributed in the tube. If $\eta_W \neq 0$, densities $N_c(t)$ and $N_A(r, t)$ will drop with time till all molecules A are captured or annihilated on the wall.

1 Exact solution

The differential equation that describes the change of concentration $N_A(\mathbf{r}, t)$ as a function of spatial position \mathbf{r} and time t is given by [2]:

$$D_{AB} \nabla^2 N_A(\mathbf{r}, t) - u_{AB} \Sigma_{aAB} N_A(\mathbf{r}, t) + S_A(\mathbf{r}, t) = \partial N_A(\mathbf{r}, t) / \partial t. \quad (1)$$

For a cylindrical tube of length L much larger than the radius R , (1) simplifies to:

$$D_{AB} \left\{ \partial^2 N_A(r, t) / \partial r^2 + r^{-1} \partial N_A(r, t) / \partial r \right\} - u_{AB} \Sigma_{aAB} N_A(r, t) + S_A(r, t) = \partial N_A(r, t) / \partial t. \quad (2)$$

Here: D_{AB} , diffusion coefficient for molecules A diffusing through a medium of (primarily) molecules B (cm^2/s); u_{AB} , mean encounter velocity of molecules A relative to molecules B in the gas (cm/s); Σ_{aAB} , removal coefficient (by chemical reaction or deexcitation) for molecules A in the gas phase (*not on walls*) due to collisions with molecules B (cm^{-1});

r , radial distance from the tube axis (cm); N_A , N_B , density of molecules A and B, respectively, (cm^{-3}); $S_A(r, t)$, production rate of molecules A in the gas phase, (molecules A $\text{cm}^{-3} \text{s}^{-1}$).

From the kinetic theory of gases one has that [3, 4]:

$$D_{AB} = u_{AB}/(3N_B\sigma_{AB}) \\ = 3.60T^{3/2}(\text{K})/\{M_{AB}^{1/2}(\text{amu})\sigma_{AB}(\text{\AA}^2)p_B(\text{Torr})\}(\text{cm}^2/\text{s}); \quad (3)$$

$$u_{AB} = \{(8/\pi)(kT/M_{AB})\}^{1/2} \\ = 1.457 \times 10^4 T^{1/2}(\text{K})M_{AB}^{-1/2}(\text{amu})(\text{cm}/\text{s}); \quad (4)$$

$$\Sigma_{aAB} = \sigma_{aAB}N_B = \mathcal{P}_a\sigma_{AB}N_B(\text{cm}^{-1}); \quad (5)$$

$$M_{AB} = M_A M_B / (M_A + M_B)(\text{amu}). \quad (6)$$

In (3)–(6): T is the gas temperature (K); $p_B \approx p_{\text{tot}}$ is the gas pressure of B (Torr); M_A and M_B are the masses of molecules A and B (amu = atomic mass units); and σ_{aAB} is the reaction/attachment/deexcitation cross-section (cm^2) in the gas for molecules A encountering molecules B. This cross-section can be written as the product $\mathcal{P}_a\sigma_{AB}$, where σ_{AB} is the average encounter cross-section (cm^2) for molecules A colliding with molecules B, and \mathcal{P}_a is the probability for molecules A to attach/deexcite/react with molecules B in gas-phase encounters. The density N_X of molecules X in a gas can be expressed in terms of pressure and temperature by the gas law:

$$N_X = 0.953 \times 10^{19} p_X(\text{Torr})T^{-1}(\text{K}) (\text{molecules X cm}^{-3}). \quad (7)$$

Assuming first that $\Sigma_{aAB} = 0$, we solve (2) for the case that molecules A are created at $t = 0$, and the initial distribution is: (a) a line source, i.e. all A are at $r = 0$ at $t = 0$; or (b) all molecules A are uniformly distributed at constant density between $r = 0$ and $r = R$ at $t = 0$.

1.1 Line source

For case (a), one can write for the source term $S_A(r, t) = N_0\delta(r)\delta(t)$, where $\delta(x)$ is the delta function with $\int \delta(x)dx = 1$ and $\delta(x) = 0$ for $x \neq 0$. The solution of (2) is then (with $\Sigma_{aAB} = 0$):

$$N_A(r, t) = N_0 J_0(\mu r/R) \exp(-\mu^2 R^{-2} D_{AB} t) \\ (\text{molecules A cm}^{-3}), \quad (8)$$

where μ is to be determined, and $J_0(x)$ is the Bessel function of order zero. To find μ we consider the boundary conditions at the wall. At the wall $r = R$ of the cylindrical tube, one has, according to diffusion theory, that the outgoing current of molecules j_+ crossing $1 \text{ cm}^2/\text{s}$ equals, to first order [2]

$$j_+ = u_A [N_A/4 - 1/2(D_{AB}/u_A)\partial N_A/\partial r]_{r=R}, \quad (9a)$$

while the incoming current j_- is:

$$j_- = u_A [N_A/4 + 1/2(D_{AB}/u_A)\partial N_A/\partial r]_{r=R}. \quad (9b)$$

Here u_A is the mean random velocity of molecules A in the gas relative to a stationary wall:

$$u_A = \{(8/\pi)(kT/M_A)\}^{1/2} \\ = 1.457 \times 10^4 T^{1/2}(\text{K})M_A^{-1/2}(\text{amu})(\text{cm}/\text{s}), \quad (10)$$

which is the same as (4) except M_A is substituted for M_{AB} . If one assumes that a fraction η_W sticks to the wall, and $(1 - \eta_W)$ returns into the gas after striking the wall, one has:

$$j_- = (1 - \eta_W)j_+, \quad (11)$$

or, using (9) and (11):

$$[N_A + 2(D_{AB}/u_A)\partial N_A/\partial r]_{r=R} = \\ (1 - \eta_W)[N_A - 2(D_{AB}/u_A)\partial N_A/\partial r]_{r=R}. \quad (12)$$

The derivative of the Bessel function $J_0(\mu r/R)$ is given by [5]:

$$dJ_0(\mu r/R)/dr = (-\mu/R)J_1(\mu r/R), \quad (13)$$

in which $J_1(x)$ is the Bessel function of first-order. When (8) and (13) are substituted into (12), the desired solution for μ can be found from the transcendental equation:

$$hJ_0(\mu) = \mu J_1(\mu) \rightarrow h = \mu J_1(\mu)/J_0(\mu) \\ = f(\mu) \rightarrow \mu = f^{inv}(h), \quad (14)$$

where $f^{inv}(h)$ is the inverse function of $f(\mu) = h$ plotted in Fig. 1, and h equals:

$$h = 1/2R(u_A/D_{AB})\eta_W/(2 - \eta_W) \\ = 1.5(R/\lambda_c)\eta_W/(2 - \eta_W) \\ = 1430(M_{AB}/M_A)^{1/2}p_B\sigma_{AB}RT^{-1}\eta_W/(2 - \eta_W) \\ (\text{Torr}, \text{\AA}^2, \text{cm}, \text{K}). \quad (15)$$

Here (3) and (4) were used and the mean-free-path for collisions λ_c is defined here as:

$$\lambda_c = 3D_{AB}/u_A = (M_A/M_{AB})^{1/2}(N_B\sigma_{AB})^{-1} \\ = (M_A/M_{AB})^{1/2}T(\text{K})/[953p_B(\text{Torr})\sigma_{AB}(\text{\AA}^2)](\text{cm}). \quad (16)$$

Thus, after calculating the constant h from (15), one can obtain μ from (14) by trial and error, or from Fig. 1. The dimensionless physical constant h represents a group of transport and geometry parameters which determine the value of $\mu = \mu(h)$. We shall need $\mu = \mu(h)$ below, since we want to determine $k_W = k_W(\mu) = k_W(h)$ directly as a function of h .

The net loss rate of molecules A striking the wall is, from (9a) and (9b):

$$j_{\text{net}} = j_- - j_+ = D_{AB}(\partial N_A/\partial r)_{r=R}. \quad (17)$$

Then the loss rate of molecules A across surface area $2\pi RL$ surrounding volume $\pi R^2 L$ is:

$$k_W L \int_0^R \{N_A(r)2\pi r\}dr = -2\pi R L D_{AB}(\partial N_A/\partial r)_{r=R},$$

or

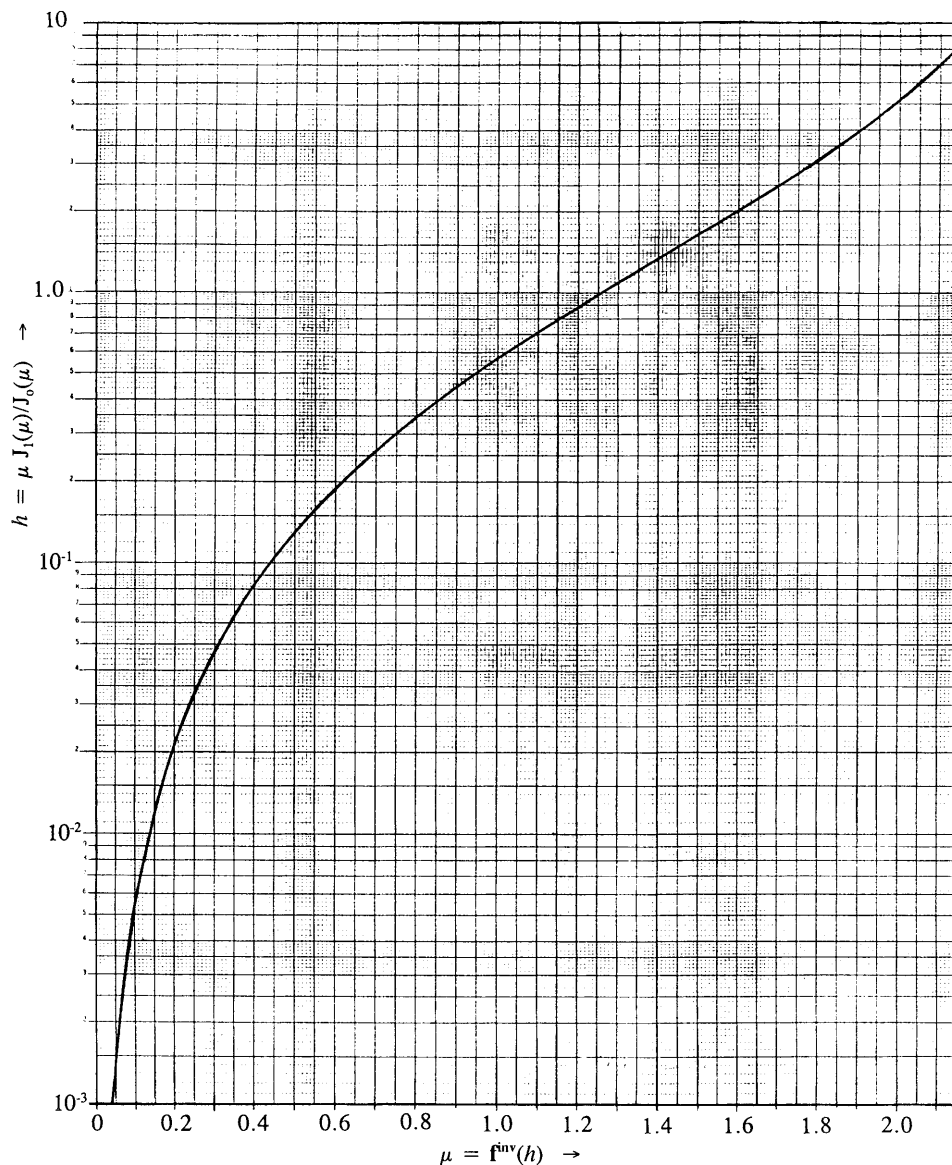


Fig. 1. Plot of relation between μ and h

$$k_W = -RD_{AB}(\partial N_A/\partial r)_{r=R} / \left[\int_0^R \{N_A(r)r\} dr \right] (\text{s}^{-1}). \quad (18)$$

Here k_W is the fraction of molecules A lost per second from volume $\pi R^2 L$, which equals the average rate for a molecule A in the tube to be captured by the wall. Now $N_A(r, t)$ was given by (8), and since for the Bessel function $J_0(x)$ one has the relations [5]

$$dJ_0(x)/dx = -J_1(x), \quad (19a)$$

and

$$\int_0^x J_0(x) dx = xJ_1(x), \quad (19b)$$

one finds from (8), (18) and (19) that the wall reach and capture rate equals:

$$k_W = D_{AB}(\mu/R)^2 (\text{s}^{-1} \text{ per molecule A}). \quad (20)$$

As expected, k_W is precisely equal to the decay coefficient of the exponential time-dependent part of (8), if the bulk absorption $\Sigma_{aAB} = 0$. The results (14), (15) and (20) are essentially the same as obtained previously by Margottin-Maclou et al. [1].

At moderate pressures $p_{\text{tot}} \geq 1$ Torr, one finds that $h \gg 1$, for the case that $\eta_W > 0.1$. One then has from (14):

$$J_0(\mu) = (\mu/h)J_1(\mu) \approx 0, \quad (21)$$

which yields $\mu = 2.405$. Using this value of μ as reference, one can rewrite (20) in the form:

$$k_W = (2.405)^2 (\mu/2.405)^2 D_{AB}/R^2 \\ = [29.3T^{3/2}/(R^2 p_B \sigma_{AB} M_{AB}^{1/2})] F(\eta_W) (\text{s}^{-1}), \quad (22)$$

or for the average migration time τ_W for molecule A to reach the wall:

$$\begin{aligned}\tau_W &= k_W^{-1} = (R/2.405)^2 / \{D_{AB}F(\eta_W)\} \\ &= R^2 p_B \sigma_{AB} M_{AB}^{1/2} / \{29.3 T^{3/2} F(\eta_W)\} (s).\end{aligned}\quad (23)$$

Here we used (3) and we define:

$$\begin{aligned}F(\eta_W) &= (\mu/2.405)^2 = \{f^{inv}(h)/2.405\}^2 \\ &= \{f^{inv}(\eta_W)/2.405\}^2,\end{aligned}\quad (24)$$

whose value ranges between 0 and 1, that is $0 \leq F(\eta_W) \leq 1$. For $\eta_W > 0.1$, $F(\eta_W) \approx 1$ in (23). For $\eta_W < 0.1$, μ and thus $F(\eta_W)$ can be obtained from (14) or Fig. 1.

Returning to (2), if $\Sigma_{aAB} \neq 0$, the solution of $N_A(r, t)$ with $S_A = \delta(t)\delta(r)$ is:

$$\begin{aligned}N_A(r, t) &= N_o J_o(\mu r/R) \exp\{-(k_W + u_{AB} \Sigma_{aAB})t\} \\ &\quad (\text{molecules A cm}^{-3}),\end{aligned}\quad (25)$$

where μ is given by (14), k_W by (20), u_{AB} by (4), and Σ_{aAB} by (5). Thus if $\Sigma_{aAB} \neq 0$, there is an additional gas-phase loss factor f_a for molecules A, given by:

$$f_a = \exp(-u_{AB} \Sigma_{aAB} t). \quad (26)$$

For example, if molecules A are laser-excited species A* that lose their excitation upon striking the wall, additional excitation losses from collisions with B's are accounted for by the factor f_a .

1.2 Constant volume source

In most practical cases, the original density distribution N_o of molecules A at $t = 0$ is not a line source $N_o\delta(r)$, but is closer to being a constant between $r = 0$ and $r = R$ at $t = 0$. That is, case (b) applies and the source term S_A is given by:

$$S_A(r, t) = N_o \delta(t) H(R - r) = N_o \delta(t) H(1 - x). \quad (27)$$

Here

$$x = r/R, \quad (28)$$

and the Heaviside unit step function $H(y)$ is defined by

$$H(y) = 1 \quad \text{for } y \geq 0, \text{ and } H(y) = 0 \quad \text{for } y < 0. \quad (29)$$

The solution of (2) with source term (27) and boundary condition $N_A = 0$ for $x \geq 1$, can be obtained by expanding the constant N_o as a Fourier series of Bessel functions $J_o(\mu_n x)$:

$$N_o = N_o \sum_{n=1}^{\infty} \{a_n J_o(\mu_n x)\}, \quad (30)$$

with

$$a_n = 2 / \{\mu_n J_1(\mu_n)\}, \quad (31)$$

where the μ_n are values for "zeros" of the oscillating function $J_o(\mu_n) = 0$. Table 1 lists the first 40 values of μ_n and coefficients a_n [5].

Table 1. Bessel-function Fourier expansion coefficients

n	μ_n	$J_1(\mu_n)$	a_n	n	μ_n	$J_1(\mu_n)$	a_n
1	2.4048	+0.5191	+1.6021	21	65.1900	+0.09882	+0.3105
2	5.5201	-0.3403	-1.0647	22	68.3315	-0.09652	-0.3032
3	8.6537	+0.2751	+0.8513	23	71.4730	+0.09438	+0.2965
4	11.7915	-0.2325	-0.7295	24	74.6145	-0.09237	-0.2902
5	14.9309	+0.2065	+0.6487	25	77.7560	+0.09049	+0.2842
6	18.0711	-0.1877	-0.5896	26	80.8976	-0.08871	-0.2787
7	21.2116	+0.1733	+0.5441	27	84.0391	+0.08704	+0.2734
8	24.3525	-0.1617	-0.5079	28	87.1806	-0.08545	-0.2685
9	27.4935	+0.1552	+0.4780	29	90.3222	+0.08396	+0.2638
10	30.6346	-0.1442	-0.4527	30	93.4637	-0.08253	-0.2593
11	33.7758	+0.1373	+0.4313	31	96.6053	+0.08118	+0.2550
12	36.9171	-0.1313	-0.4126	32	99.7468	-0.07989	-0.2510
13	40.0584	+0.1261	+0.3959	33	102.8884	+0.07866	+0.2471
14	43.1998	-0.1214	-0.3814	34	106.0299	-0.07749	-0.2434
15	46.3412	+0.1172	+0.3682	35	109.1715	+0.07636	+0.2399
16	49.4826	-0.1134	-0.3564	36	112.3131	-0.07529	-0.2365
17	52.6241	+0.1100	+0.3455	37	115.4546	+0.07426	+0.2333
18	55.7655	-0.1068	-0.3358	38	118.5962	-0.07327	-0.2302
19	58.9070	+0.1040	+0.3265	39	121.7377	+0.07232	+0.2272
20	62.0485	-0.1013	-0.3182	40	124.8793	-0.07140	-0.2243

The solution $N_A(r, t)$ with $S_A = N_o\delta(t)H(R - r)$, and assuming $F(\eta_W) = 1$, is, then

$$\begin{aligned}N_A(r, t)/N_o &= \sum_{n=1}^{\infty} [a_n J_o(\mu_n r/R) \\ &\quad \times \exp\{-(D_{AB}\mu_n^2/R^2 + u_{AB}\Sigma_{aAB})t\}], \\ &\quad \text{for } 1 < \eta_W < 0.1,\end{aligned}\quad (32)$$

while the wall attachment rate per molecule A according to (18) is now:

$$\begin{aligned}k_W &= (D_{AB}/R^2) \left[\frac{\sum_n \{\mu_n a_n J_1(\mu_n) \exp(-\mu_n^2 R^{-2} D_{AB} t)\}}{\sum_n \{\mu_n^{-1} a_n J_1(\mu_n) \exp(-\mu_n^2 R^{-2} D_{AB} t)\}} \right] / \\ &\quad (s^{-1}), \\ &\quad \text{for } 0.1 < \eta_W < 1.\end{aligned}\quad (33)$$

It must be emphasized that (32) and (33) are based on the assumption that $N_A(r = R, t) \approx 0$ at the wall ($r = R$) and that the wall sticking probability $\eta_W > \sim 0.1$ as discussed before.

If the wall sticking probability $\eta_W < 0.1$, the value of $N_A(r, t)$ is finite at $r = R$. In this case one can define an extrapolated radius R_e (with $R_e > R$) at which the analytic continuation of the function $N_A(r, t)$ goes to 0 and thereby also all Bessel functions $J_o(\mu_n r/R_e)$. Imposing boundary condition (12) again on $N_A(r, t)$, assuming now that all $J_o(\mu_n r/R_e)$ vanish at $r = R_e$, one obtains:

$$\begin{aligned}h &= \left[\frac{\sum_n \{g \mu_n a_n J_1(g \mu_n) \exp(-g^2 \mu_n^2 R^{-2} D_{AB} t)\}}{\sum_n \{a_n J_o(g \mu_n) \exp(-g^2 \mu_n^2 R^{-2} D_{AB} t)\}} \right] / \\ &\quad (34)\end{aligned}$$

where h again equals the physical constant given by (15), the μ_n and a_n are still given by the values listed in Table 1, and

the parameter g is defined by:

$$g = R/R_e \quad (0 < g < 1). \quad (35)$$

Then k_W equals:

$$k_W = g^2(D_{AB}/R^2) \left[\sum_n \{ \mu_n a_n J_1(g\mu_n) \times \exp(-g^2 \mu_n^2 R^{-2} D_{AB} t) \} \right] / \left[\sum_n \{ \mu_n^{-1} a_n J_1(g\mu_n) \exp(-g^2 \mu_n^2 R^{-2} D_{AB} t) \} \right] \quad (s^{-1}), \text{ for } 0 < \eta_W < 0.1. \quad (36)$$

An inspection of (34) shows that g must depend on t , if there is to be a unique solution of g in terms of h . That is, in principle, by inverting (34) using a computer, one can obtain:

$$g = g(h, t). \quad (37)$$

Since the tube radius R is a constant and h is a constant, only the extrapolated radius R_e can vary with time, that is $R_e = R_e(t)$. At time $t = 0$, one has $g = g_0$ as determined by the equation:

$$h = \left[\sum_n \{ g_0 \mu_n a_n J_1(g_0 \mu_n) \} \right] / \left[\sum_n \{ a_n J_0(g_0 \mu_n) \} \right] \quad (\text{at } t = 0). \quad (38)$$

Solving for $g = g(t)$ from (34) would be rather cumbersome. Fortunately, inspection of the terms $\exp(-g^2 \mu_n^2 R^{-2} D_{AB} t)$ in (34) and (36) shows that after the original injection of a batch charge of N_0 molecules/cm³ at $t = 0$, most higher-order terms in the Bessel function series (32) dampen out quickly within a fraction of the time constant τ_W given by (23) with $F(\eta_W) = 1$. For example, the first three time decay terms with $n = 1$, $n = 2$, and $n = 3$, are $\exp(-t/\tau_W)$, $\exp(-5.25t/\tau_W)$, and $\exp(-12.95t/\tau_W)$. Thus, all terms except $n = 1$ in the Bessel series expansion can be neglected when $t > 0.2\tau_W$. Unless one must know the transient changes of $N_A(r, t)$ during the time interval $0 < t < 0.2\tau_W$, one can use (22) obtained for case (a) to calculate diffusional loss rates for case (b) without great error. In summary, after a brief transient period $\Delta t \sim 0.2\tau_W$ the constant density $N_A(r) = N_0$ at time $t = 0$ changes into a Bessel function distribution $N_A(r) = N_0 J_0(\mu^* r/R)$. Here $\mu^* = f^{inv}(h)$ is the solution of μ from (14).

2 Approximate closed-form solution

Instead of solving (14) with the use of Fig. 1, a convenient approximate solution can be obtained with Amaldi and Fermi's albedo theory according to which the linear extrapolation length $d_e = R_e - R$ is approximately [6]:

$$d_e = (2/3)\lambda_c(2 - \eta_W)/\eta_W = (2D_{AB}/u_A)(2 - \eta_W)/\eta_W = R/h \quad (39)$$

where h was given by (15). Then:

$$g = R/R_e = R/(R + d_e) = (1 + h^{-1})^{-1} = [1 + 2D_{AB}R^{-1}u_A^{-1}(2 - \eta_W)/\eta_W]^{-1} = [1 + (2/3)(\lambda_c/R)(2 - \eta_W)/\eta_W]^{-1} \quad (40)$$

in which (3) and (4) were used. The rate k_W is then:

$$k_W = (g\mu_1/R)^2 D_{AB} = (\mu_1/R)^2 D_{AB} / [1 + (2/3)(\lambda_c/R)(2 - \eta_W)/\eta_W]^2 = [29.3T^{3/2}/(R^2 p_B \sigma_{AB} M_{AB}^{1/2})] / [1 + \{7 \times 10^{-4}(M_A/M_{AB})^{1/2} T / (p_B \sigma_{AB} R)\}(2 - \eta_W)/\eta_W]^2 \quad (s^{-1}) \text{ (albedo approximation)}, \quad (41)$$

where $\mu_1 = 2.4048$. Comparing (41) with (22), note that for the albedo approximation:

$$F(\eta_W) = g^2 = (1 + h^{-1})^{-2} \text{ (albedo approximation)}. \quad (42)$$

For small μ , one finds from (14) that:

$$h = \mu J_1(\mu)/J_0(\mu) \approx 0.50\mu^2 \text{ (diffusion theory, small } \mu), \quad (43)$$

since for small μ , one can approximate [7]:

$$J_0(\mu) \approx ((1/2)\mu)^0/\Gamma(1) = 1 \text{ (for small } \mu), \quad (44)$$

$$J_1(\mu) \approx ((1/2)\mu)/\Gamma(2) = 1/2\mu \text{ (for small } \mu), \quad (45)$$

where $\Gamma(x)$ is the gamma function. Thus, according to (43):

$$\mu \approx (2h)^{1/2} \text{ (diffusion theory, small } \mu \text{ and } h). \quad (46)$$

Then, from (24):

$$F(\eta_W) = (\mu/2.405)^2 \approx 2h/(2.405)^2 = 0.346h \text{ (diffusion theory, small } \mu \text{ and } h). \quad (47)$$

In the albedo approximation, on the other hand, it is apparent from (42) that:

$$F(\eta_W) = g^2 = (1 + h^{-1})^{-2} \approx h^2, \text{ for } h \ll 1 \text{ (albedo approximation, small } h), \quad (48)$$

and

$$F(\eta_W) = g^2 = (1 + h^{-1})^{-2} \approx \{1 + (0.500h)^{-1}\}^{-1}, \text{ for } h \gg 1 \text{ (albedo approx, large } h). \quad (49)$$

Comparing (48) and (47), it is clear that as $h \rightarrow 0$, $F(\eta_W)$ tends to 0 more rapidly in the albedo approximation than in diffusion theory. For $h \gg 1$ (i.e. high gas pressures), both theories correctly give $F(\eta_W) \rightarrow 1$, according to (14), (24) and (42). Considering that the albedo approximation is better at higher values of h , while diffusion theory is better for low h , a compromise between diffusion and albedo equations can be obtained using the expression:

$$F(\eta_W) = F(h) \approx \{1 + (0.346h)^{-1}\}^{-1} \text{ (diffusion/albedo compromise approximation)}. \quad (50)$$

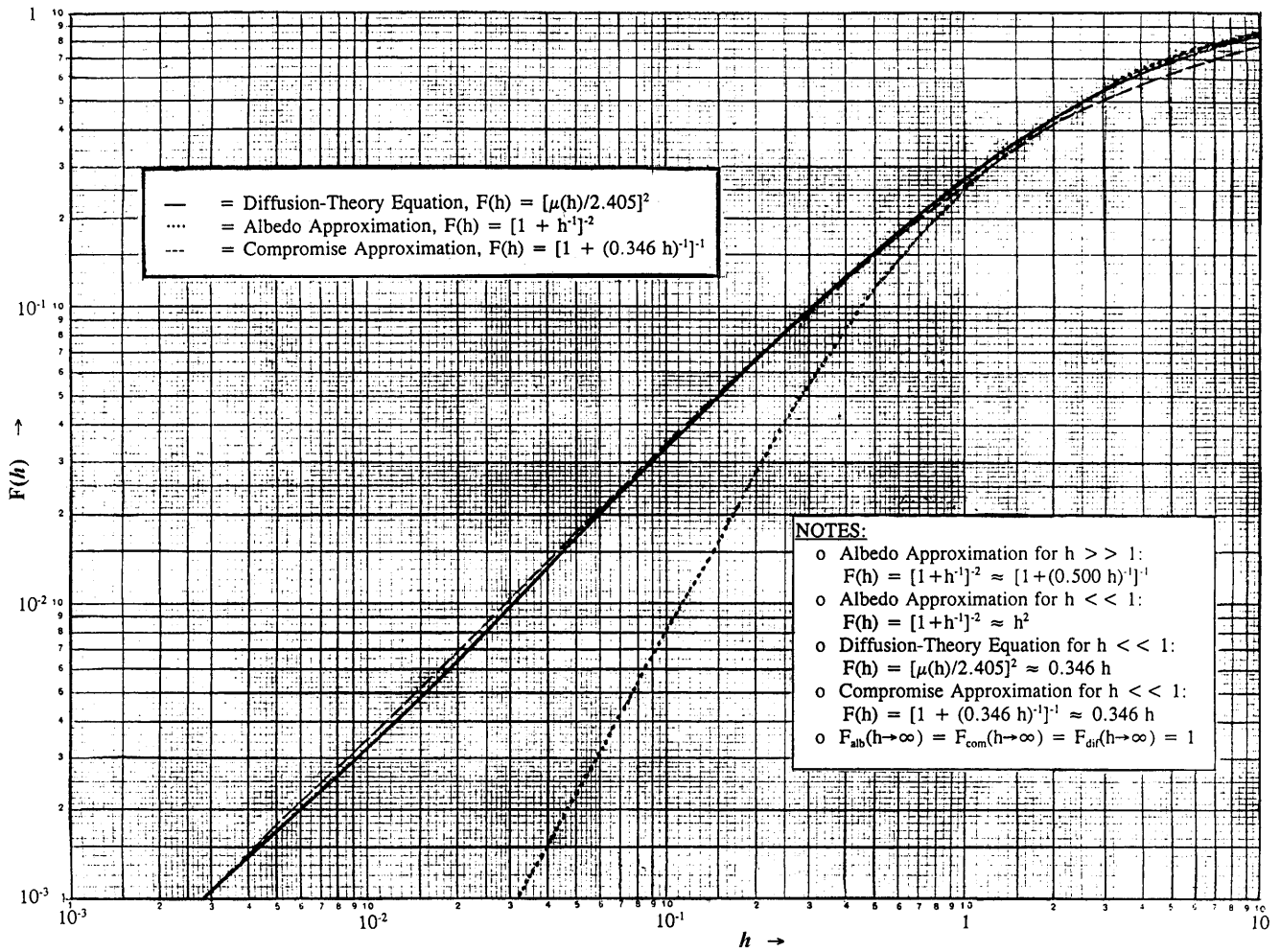


Fig. 2. Comparison of exact and approximate functions $F(h)$

Equation (50) becomes equal to the diffusion relation (47) for $h \ll 1$, while for larger values of h , it is close to (49) except that the coefficient 0.346 replaces the value 0.500. This causes $F(\eta_W) = F(h)$ to be overestimated by 2.8% at $h = 1$ and underestimated by 6% at $h = 10$, when compared with the albedo (42). It correctly yields $F(\eta_W) = F(h) = 1$ as $h \rightarrow \infty$, and is easier to use than calculations involving inverse determinations of μ from (14) or Fig. 1. Figure 2 compares plots of the albedo approximation (42), the compromise approximation (50), and the exact diffusion-theory curve for $F(h)$ given by (24). Clearly (50) is a fairly good fit for the exact diffusion-theory curve. Using (50) in (22) gives, finally:

$$\begin{aligned}
 k_W &= (2.405)^2 (D_{AB}/R^2) F(\eta_W) \\
 &\approx (2.405)^2 (D_{AB}/R^2) \{1 + (0.346h)^{-1}\}^{-1} \\
 &= [29.3T^{3/2}/(R^2 p_B \sigma_{AB} M_{AB}^{1/2})] \{1 \\
 &\quad + \{2.02 \times 10^{-3} (M_A/M_{AB})^{1/2} T / \\
 &\quad (p_B \sigma_{AB} R)\} (2 - \eta_W)/\eta_W\}^{-1} \text{ (s}^{-1}\text{)} \\
 &\text{(diffusion/albedo compromise approximation).} \quad (51)
 \end{aligned}$$

Here we inserted expressions (3) and (15) into the last part of (51). Equation (51) is a very useful result that provides an explicit expression for k_W or $\tau_W = k_W^{-1}$ for molecular migration from a line or uniform source of molecules in a long tube.

A plot of (51), with k_W as a function of η_W , is shown in Fig. 3 for the diffusion of nitrogen-diluted UF_6 molecules in a long tube with $R = 1$ cm at $T = 250$ K and various gas pressures $p_B \approx p_{\text{tot}}$. The only physical parameter that is usually not known precisely is the sticking coefficient η_W . If a surface adsorption, condensation, or reaction is under consideration, this parameter is determined by surface physics and may vary with time depending on the nature of the wall material and wall-deposit build-up.

Note that for small values of p_B and/or η_W , the rate k_W in (51) reduces to:

$$\begin{aligned}
 k_W &= 1/2 \eta_W u_A / R = 7285 \eta_W (T/M_A)^{1/2} / R \text{ (s}^{-1}\text{)}, \\
 \text{if } \eta_W p_B &\ll \sim (M_A/M_{AB})^{1/2} T / (250 \sigma_{AB} R), \quad (52)
 \end{aligned}$$

while for $\eta_W p_B \gg \sim (M_A/M_{AB})^{1/2} T / (250 \sigma_{AB} R)$:

$$\begin{aligned}
 k_W &= (2.405)^2 D_{AB}/R^2 = (1/3)(2.405)^2 u_A \lambda_c / R^2 \\
 &= 29.3 T^{3/2} / (p_B R^2 \sigma_{AB} M_{AB}^{1/2}) \text{ (s}^{-1}\text{)}. \quad (53)
 \end{aligned}$$

3 Laminar flow

So far, it was tacitly assumed that the state of the gas in the tube is stagnant, as in a batch process. If the gas flows through

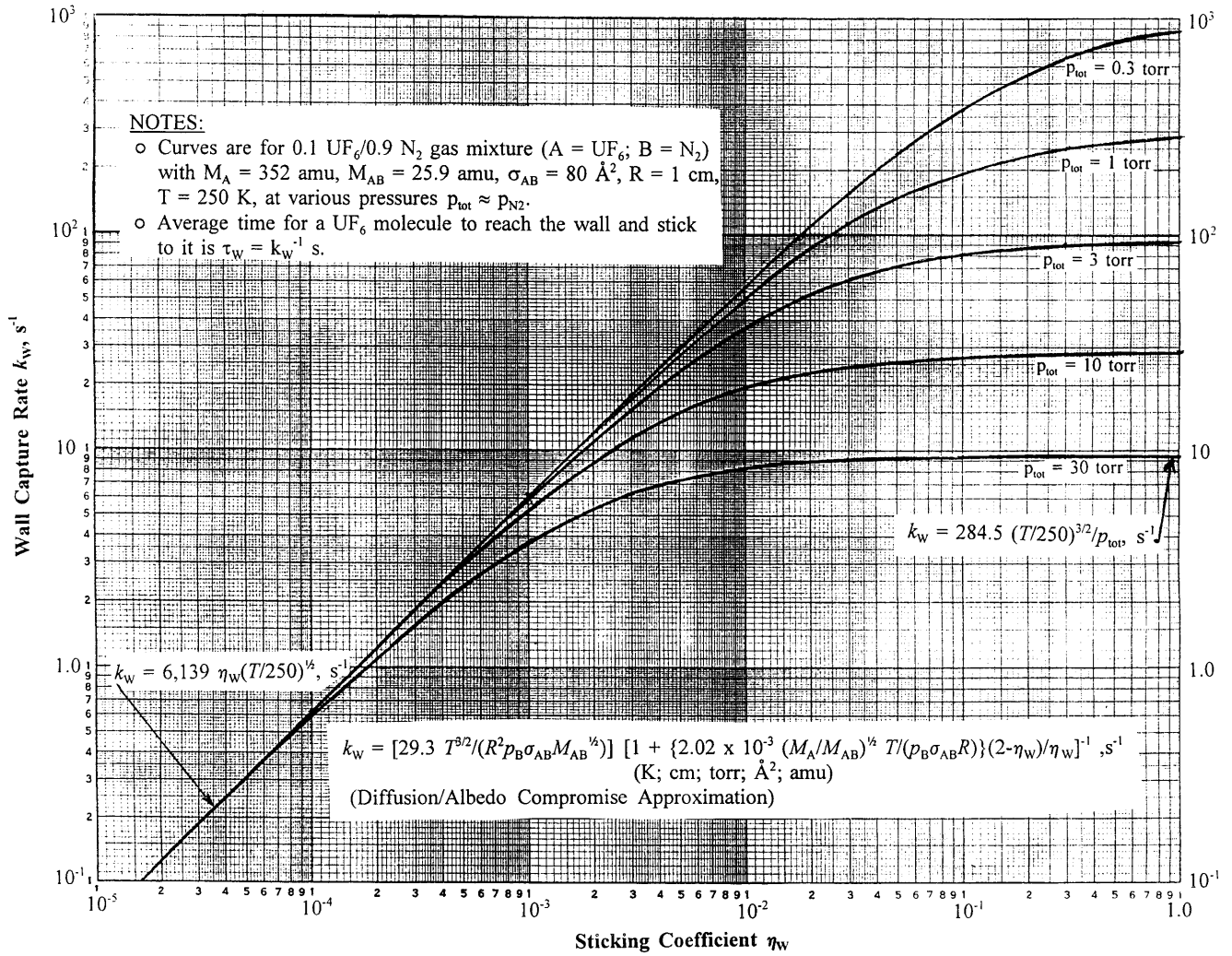


Fig. 3. Wall capture rates for gaseous UF₆ molecules in long cylindrical tube

a tube under laminar flow conditions in a continuous flow-through process, and if at the entrance (at $z = 0$), $N_A(r, z)$ is assumed to have a constant value N_0 for $0 < r < R$, this density distribution will change downstream into a Bessel-function distribution $J_0(\mu r/R)$, just like in a batch operation. One can still use all previous expressions by substituting

$$t = z/U, \quad (54)$$

where z is the gas travel distance along the tube axis, and U is the macroscopic bulk flow velocity (cm/s) along the tube axis. With (54), all time-dependent expressions $N_A(r, t)$ and $k_W(t)$ change to $N_A(r, z)$ and $k_W(z)$. As in the batch case, $N_A(r, z = 0) = N_0$ changes into a radial Bessel-function distribution $N_A(r) = N_0 J_0(\mu^* r/R)$ during travel time $\Delta t_{\text{transient}} \approx 0.2 \tau_W$, corresponding to a travel distance $\Delta z_{\text{transient}} = 0.2 U \tau_W$. Without a Bessel-function radial gradient, and a constant uniform density $N_A(r) = N_0$ at time $t = 0$ or $z = 0$, the initial rate k_W at $t = 0$ is:

$$\begin{aligned} k_W(t = 0) &= (1/2) \eta_W u_A / R \\ &= 7285 \eta_W T^{1/2} (\text{K}) / [R(\text{cm}) M_A^{1/2} (\text{amu})] (\text{s}^{-1}), \\ &\text{for } N_A(r) = N_0 = \text{constant}, \end{aligned} \quad (55)$$

since the molecular current j_+ impinging on the wall equals $j_+ = (1/4) u_A N_0$, and a fraction η_W of wall-striking molecules stick to the wall. This result, as it should be, is the same as (52) for the general case in the limit that $\eta_W p_B \ll \sim (M_A/M_{AB})^{1/2} T / (250 \sigma_{AB} R)$, except $\eta_W p_B$ is unrestricted. Note, finally, that according to (25), the drop in concentration $N_c(z) = N_A(r = 0, z)$ along the tube axis is:

$$N_c(z) = N_0 \exp\{-(k_W + u_{AB} \Sigma a_{AB})(z/U)\}, \quad (56)$$

where k_W and u_{AB} are given by (22) or (51) and (4).

4 Turbulent subsonic flow

If the gas mix flows through the tube under subsonic turbulent conditions instead of in a laminar fashion, one can no longer assume steady migration as assumed so far, since convective eddy currents and vortices are created in the gas that transport molecules "A" in bulk from the center of the tube to the walls at macroscopic speeds rather than by diffusion. Turbulence sets in generally when the Reynolds number exceeds 2100, that is:

$$\text{Re} = 2URD_{\text{BB}}^{-1} \geq 2100 \text{ (turbulent flow)}. \quad (57)$$

Here R is the tube radius (cm), U is the bulk flow velocity (cm/s), while D_{BB} (cm²/s) is the diffusion coefficient of the gas (assumed to be mostly B molecules), as before. If the scale of turbulence is sufficiently large ($Re > \sim 10000$), one can assume a radially constant concentration $N_A(r, z) = N_o(z)$. Then the average wall-capture rate k_W per molecule per second for molecules A in the tube is the same as given by (55):

$$k_W = (1/2)\eta_W u_A / R \\ = 7285 \eta_W T^{1/2} (\text{K}) / [R (\text{cm}) M_A^{1/2} (\text{amu})] (\text{s}^{-1}) \\ (\text{turbulent flow}), \quad (58)$$

with no restrictions on η_W or p_B . Though constant radially, the density of *tagged* molecules A will drop with travel distance z in accordance with (56). A comparison of (58) with (51) using typical values for T , R , p_b , M_A , and M_{AB} , shows that turbulent flow increases wall deactivation/loss rates ten- to a hundred-fold, unless $\eta_W \ll 10^{-3}$.

References

1. M. Margottin-Maclou, L. Doyenette, L. Henry: *J. Appl. Opt.* **10**, 1768 (1971); note: these authors analyzed the wall-deexcitation rate of photon-excited CO* molecules
2. S. Glasstone, M.C. Edlund: *Elements of Nuclear Reactor Theory*, Chaps. 5 and 7 (Van Nostrand, New York 1954); note: Instead of concentration N , the flux $\varphi = Nu$ is used for diffusion of neutrons, otherwise the same relations apply
3. F.W. Sears: *An Introduction to Thermodynamics, the Kinetic Theory of Gases, and Statistical Mechanics* (Addison-Wesley, Cambridge, MA 1958)
4. S. Chapman, T.G. Cowling: *Mathematical Theory of Non-Uniform Gases*, 3rd ed. (Cambridge University Press, Cambridge, GB 1988). Note: Chapman and Cowling (CC) give $D_{AB} = C_D f_D u_{AB} (N_B \sigma_{AB})^{-1}$ with u_{AB} given by (4) and constants $C_D = \pi/8 = 0.39$ (CC p. 87ff, p. 107ff) or $C_D = 3\pi/32 = 0.29$ (CC p. 258) with $f_D = 1$ for hard-sphere molecules, and other (near-unity) correction factors f_D for the Sutherland, Lennard-Jones, and some other intermolecular potentials. This compares with the simple diffusion theory value of $C_D = 1/3 = 0.33$ and $f_D = 1$ assumed in (3). To first-order, D_{AB} is independent of mole fractions of A and B (CC p. 107) and symmetric if A is exchanged with B. The mean A/B encounter velocity u_{AB} and D_{AB} in a gas must be symmetric for an interchange $A \leftrightarrow B$, because of the reciprocity requirement. Otherwise the bombardment rate $n_A u'_A \sigma_{A/B}$ by a flux of molecules A striking a target molecule B in the gas is not equal to the rate $u'_B n_A \sigma_{B/A}$ of a traveling molecule B colliding with A's. That is one *must* have $n_A u'_A \sigma_{A/B} = u'_B n_A \sigma_{B/A}$ or $u'_A = u'_B = u_{AB}$, if $\sigma_{A/B} = \sigma_{B/A}$ as required by microscopic physics. The gaseous collision term $u_{AB} \Sigma_{aAB}$ in (1) must, therefore, have velocity u_{AB} given by (4) since both A and B are mobile. However, in (9), the mean velocity u_A is for molecules A relative to a stationary wall, and in this case (10) applies
5. E. Jahnke, F. Emde: *Tables of Functions*, 4th ed. (Dover Publications, Inc., Mineola, New York 1945) p. 11 501
6. S. Glasstone, M.C. Edlund: *Elements of Nuclear Reactor Theory*, (Van Nostrand, New York 1954); note: Eq. (5.108.1) reads $d_e = (2/3)\lambda_c(1 + \beta)/(1 - \beta)$, in our case the albedo $\beta = 1 - \eta_W$
7. M. Abramowitz, I.A. Stegun: *Handbook of Mathematical Functions*, NBS Applied Mathematics Series 55, (Superintendent of Documents, US Government Printing Office, Washington DC 1964)