Mean time of diffusion- and reaction-limited loading and unloading

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Abstract

Direct determination of mean diffusion times from the Laplace transform of the spatial average of the diffusing species for $p = 0$ offers the advantage of yielding closed-form expressions rather than sum-type ones obtained otherwise from the time-dependent solution. This is made use of in the present work to determine the mean time of diffusion- and reaction-limited loading and unloading a species into or out of bodies of different shape (plate, cylinder, sphere) for the important type of boundary condition of fixed concentration in the surrounding. This approach particularly pays off for more complex cases when the calculation from the inverse of the Laplace transform becomes more and more laborious. As an example of such type, concomitant trapping and untrapping of the diffusing species within the object during unloading is considered. The obtained solutions are quantitatively discussed with examples from literature. The present concept of the mean time of loading or unloading is compared with other time constants, e.g., mean action time or time lag.

Keywords Diffusion-reaction model · Hydrogen diffusion · Characteristic time constant · Laplace transform

1 Introduction

The kinetics of diffusion-controlled loading or unloading of a species into or out of an object, e.g., a solid, with the surface in equilibrium with the surrounding, represents a standard issue of diffusion theory. Solutions for a wide variety of boundary conditions can be found in textbooks (e.g., ref. [1]). An important research field, where this issue is of particular relevance, pertains to hydrogen in host materials or more generally to ion-insertion electrodes. Diffusion theory of insertion (loading) and extraction (unloading) of hydrogen from electrodes has been elaborated in great detail, e.g., by Montella [2] and by Lee and Pyun [3] using the Laplace transform method.

An intriguing feature of this method is that it allows in a straightforward manner to derive mean values, e.g., a mean lifetime, by calculating the Laplace transform $\tilde{n}(p)$ of an appropriate function $n(t)$ for $p = 0$, rather than to derive this mean value from the solution of the diffusion model. The latter is deduced from the inverse of the Laplace transform,

a step which can be avoided for this purpose. A further particular advantage is that in this way closed-form expressions for the mean lifetime can be deduced.

Stimulated by Seeger [4], the author applied this concept in the past to positron annihilation studies of defects. Closed-form expressions of the mean positron lifetime $\overline{\tau}$ could be derived in this way for various scenarios of diffusion- and reaction-controlled trapping of positrons at extended defects, namely, at grain boundaries of spherical grains [4] with concomitant trapping at point defects [5] as well as at interfaces between matrix and cylindrical [6] or spherical precipitates [7], including spherical voids [7]. Dryzek made use of this concept for calculating the mean positron lifetime as well (e.g., ref. [8–10]).

Various approaches are used in literature to derive characteristic time scales for diffusion processes, such as first moment relaxation time constant [11, 12] and mean action time [13, 14] (see also ref. [15] and references therein), both of which represent position-dependent time scales. Another time scale is the so-called time lag [1, 16] which characterizes the long-time behavior approaching stationary flow. The mean time addressed in the present work represents a volume-averaged mean value for loading or unloading of an object. This mean value corresponds to the so-called mean residence time used to calculate drug absorption [17] (see Sect. 3).

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In the present work, closed-form expressions are derived for the mean time $\bar{\tau}$ of diffusion- and reaction-limited loading and unloading a species into or out of bodies of different shape (plate, cylinder, sphere) for the important type of boundary condition of fixed concentration in the surrounding. For comparison, mean values $\bar{\tau}$ in the form of sums (Sect. 2.2.2) are deduced from the time-dependent solution of the diffusion equation (Sect. 2.2.1), i.e., from the inverse of the Laplace transform (Sect. 2.1). As a more complex case, concomitant trapping and untrapping of the diffusing species within the object during unloading is considered (Sect. 2.3).

2 The model

2.1 Solution of diffusion equation by Laplace transformation

We consider the diffusion of a species, such as for instance hydrogen, in a plate-, cylinder-, or sphere-shaped body that is in equilibrium with the surrounding, so-called surface evaporation condition according to the textbook of Crank [1] (Fig. 1). The species in the body is characterized by the density $\rho(x, t)$ (plate) or $\rho(r, t)$ (cylinder, sphere). Laplace transformation

$$\tilde{\rho}(\mathbf{x}, p) = \int_0^\infty \exp(-pt)\rho(\mathbf{x}, t)\mathrm{d}t. \tag{1}$$

yields the diffusion equations for the plate (a), cylinder (b), and sphere (c):

$$\frac{\mathrm{d}^2\tilde{\rho}}{\mathrm{d}x^2} - \gamma^2\tilde{\rho} = -\frac{\rho_0}{D}, \tag{2a}$$

$$\frac{\mathrm{d}^2\tilde{\rho}}{\mathrm{d}r^2} + \frac{1}{r}\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}r} - \gamma^2\tilde{\rho} = -\frac{\rho_0}{D}, \tag{2b}$$

$$\frac{\mathrm{d}^2\tilde{\rho}}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}r} - \gamma^2\tilde{\rho} = -\frac{\rho_0}{D} \tag{2c}$$

with

$$\gamma^2 = \frac{p}{D} \tag{3}$$

where D denotes the diffusion coefficient and ρ_0 the constant initial concentration at time $t = 0$. If in the surrounding a constant concentration ρ_s is maintained in equilibrium, the Laplace transform of the boundary condition at the surface reads for the plate (a)
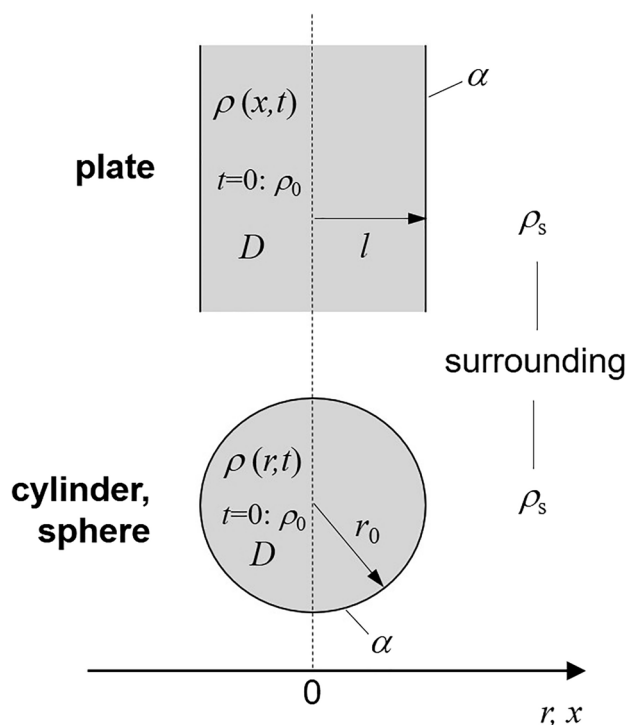

Fig. 1 Geometry of diffusion-reaction model: plate (half-thickness l), cylinder, sphere (radius r_0) with initial density ρ_0 of diffusing species embedded in a surrounding in which the density ρ_s is held constant. Temporal and spatial evolution of the concentration within the body is characterized by $\rho(x, t)$ or $\rho(r, t)$. D: diffusion coefficient; α: specific rate constant at boundary (surface)

$$D\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x}\big|_{x=l} + \alpha\left(\tilde{\rho}(l) - \frac{\rho_s}{p}\right) = 0 \tag{4a}$$

and for the cylinder and sphere

$$D\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}r}\big|_{r=r_0} + \alpha\left(\tilde{\rho}(r_0) - \frac{\rho_s}{p}\right) = 0 \tag{4b}$$

where α denotes a specific rate constant, l the half-thickness of the plate ($-l \leq x \leq l$), and r_0 the radius of the cylinder and sphere ($0 \leq r \leq r_0$). For the plate, in addition, the boundary condition

$$\frac{\mathrm{d}\tilde{\rho}}{\mathrm{d}x}\big|_{x=0} = 0 \tag{5}$$

at the midplane $x = 0$ has to be fullfilled. With the Ansatz $\tilde{\rho} = A\cosh(\gamma x) + \rho_0/p$ (plate), $\tilde{\rho} = AI_0(\gamma r) + \rho_0/p$ (cylinder, $I_i(z)$: modified Bessel function), $\tilde{\rho} = \sinh(\gamma r)/(\gamma r) + \rho_0/p$ (sphere), the diffusion equation above with the respective boundary condition can be solved. From the inverse of the Laplace transform, the solution for the plate (a), cylinder (b), and sphere (c) are obtained (see textbook [1])

$$\frac{\rho(x,t) - \rho_s}{\rho_s - \rho_0} = -\sum_{n=1}^{\infty} \frac{2L\cos(\overline{\beta}x/l)}{\cos\overline{\beta}_n(\overline{\beta}_n^2 + L^2 + L)} \exp\left(-\frac{D\overline{\beta}_n^2}{l^2}t\right),$$

(6a)

$$\frac{\rho(r,t) - \rho_s}{\rho_s - \rho_0} = -\sum_{n=1}^{\infty} \frac{2LJ_0(\overline{\beta}_n r/r_0)}{J_0(\overline{\beta}_n)(\overline{\beta}_n^2 + L^2)} \exp\left(-\frac{D\overline{\beta}_n^2}{r_0^2}t\right),$$

(6b)

with Bessel functions $J_i(z)$ of order i,

$$\frac{\rho(r,t) - \rho_s}{\rho_s - \rho_0} = -\sum_{n=1}^{\infty} \frac{2Lr_0\sin(\overline{\beta}_n r/r_0)}{r\sin\overline{\beta}_n(\overline{\beta}_n^2 + L(L-1))} \exp\left(-\frac{D\overline{\beta}_n^2}{r_0^2}t\right),$$

(6c)

where $\overline{\beta}_n$ denotes the roots of

$$\overline{\beta}_n\tan\overline{\beta}_n = L,$$

(7a)

$$-\overline{\beta}_n J_1(\overline{\beta}_n) + LJ_0(\overline{\beta}_n) = 0,$$

(7b)

$$\overline{\beta}_n\cot\overline{\beta}_n + L - 1 = 0.$$

(7c)

with $\beta^2 = -\overline{\beta}^2$, $\beta = \gamma l$ (plate), $\beta = \gamma r_0$ (cylinder, sphere), and

$$L = \frac{\alpha l}{D}$$

(8a)

for the plate and

$$L = \frac{\alpha r_0}{D}$$

(8b)

for the cylinder and sphere.

2.2 Mean time of diffusion-limited loading and unloading

2.2.1 Direct determination of mean time from Laplace transform

The above quoted solutions are derived from the respective Laplace transform $\tilde{\rho}(x,p)$ or $\tilde{\rho}(r,p)$, which reads for the plate (a), cylinder (b), and sphere (c):

$$\tilde{\rho}(x,p) = \frac{\alpha(\rho_s - \rho_0)\cosh(\gamma x)}{p(\alpha\cosh(\beta) + D\gamma\sinh(\beta))} + \frac{\rho_0}{p}$$

(9a)

$$\tilde{\rho}(r,p) = \frac{\alpha(\rho_s - \rho_0)r_0}{pD(\beta I_1(\beta) + LI_0(\beta))}I_0(\gamma r) + \frac{\rho_0}{p},$$

(9b)

$$\tilde{\rho}(r,p) = \frac{\alpha(\rho_s - \rho_0)\beta r_0}{pD\sinh\beta(\beta\coth\beta + L - 1)}\frac{\sinh(\gamma r)}{\gamma r} + \frac{\rho_0}{p}$$

(9c)

with $\beta = \gamma l$ for the plate and $\beta = \gamma r_0$ for cylinder and sphere.

For calculation of the mean time of unloading, we consider the spatial average by integration of $\tilde{\rho}(x,p)$ ($\tilde{\rho}(r,p)$), which yields for the plate (a), cylinder (b), and sphere (c):

$$\tilde{n}(p) = \frac{1}{l\rho_0}\int_0^l \tilde{\rho}(x,p)\mathrm{d}x,$$

(10a)

$$\tilde{n}(p) = \frac{1}{\pi r_0^2\rho_0}\left(2\pi\int_0^{r_0} \tilde{\rho}(r,p)r\mathrm{d}r\right),$$

(10b)

$$\tilde{n}(p) = \frac{1}{4/3\pi r_0^3\rho_0}\left(4\pi\int_0^{r_0} \tilde{\rho}(r,p)r^2\mathrm{d}r\right).$$

(10c)

The spatial integral $\tilde{n}(p)$ represents the Laplace transform

$$\tilde{n}(p) = \int_0^{\infty} \exp(-pt)n(t)\mathrm{d}t$$

(11)

of the fraction $n(t)$ of diffusion species which is still present at time t. The mean lifetime of the diffusing species, i.e., the mean time of unloading, is given by

$$\overline{\tau} = \int_0^{\infty}\left(-\frac{\mathrm{d}n}{\mathrm{d}t}\right)t\mathrm{d}t.$$

(12)

Partial integration

$$\overline{\tau} = \int_0^{\infty} n(t)\mathrm{d}t = \tilde{n}(p=0)$$

(13)

shows that $\overline{\tau}$ is given by the Laplace transform (Eq. 11) at $p = 0$ in the case of complete unloading ($\rho_s = 0$) [4].

Calculating the mean time of unloading for $\rho_s > 0$, one has to consider the fraction $\tilde{n}_{ex}(p)$ in excess to the concentration ρ_s in the surrounding, which is obtained by replacing in the integral $\tilde{\rho}(r,p)$ by ($\tilde{\rho}(r,p) - \rho_s/p$). Correspondingly, in the prefactor for normalization ρ_0 has to be replaced by $\rho_0 - \rho_s$. Integrating with this substitution yields for the plate (a), cylinder (b), and sphere(c):

$$\tilde{n}_{ex}(p) = -\frac{\alpha l}{D}\frac{\sinh(\beta)}{p\beta(L\cosh(\beta) + \beta\sinh(\beta))} + \frac{1}{p}$$

(14a)

$$\tilde{n}_{ex}(p) = -\frac{2\alpha r_0}{D}\frac{I_1(\beta)}{p\beta(\beta I_1(\beta) + LI_0(\beta))} + \frac{1}{p},$$

(14b)

$$\tilde{n}_{ex}(p) = -\frac{3\alpha}{r_0}\frac{\beta\coth\beta - 1}{p^2(\beta\coth\beta + L - 1)} + \frac{1}{p}. \tag{14c}$$

The mean time $\overline{\tau}$ of unloading from ρ_0 down to ρ_s is given by

$$\overline{\tau} = \tilde{n}_{ex}(p = 0). \tag{15}$$

Taylor expansion of the β-dependent functions in Eq. (14) and finally taking into account $\beta^2 = pl^2/D$ (plate) or $\beta^2 = pr_0^2/D$ (cylinder, sphere) yields for the mean unloading time of plate (a), cylinder (b), and sphere (c) after some algebra:

$$\overline{\tau} = \frac{l^2}{3D} + \frac{l}{\alpha}, \tag{16a}$$

$$\overline{\tau} = \frac{r_0^2}{8D} + \frac{r_0}{2\alpha}, \tag{16b}$$

$$\overline{\tau} = \frac{r_0^2}{15D} + \frac{r_0}{3\alpha}. \tag{16c}$$

The calculation of the mean loading time from an initial value $\rho_0 = 0$ up to the density ρ_s in the surrounding is done in an analogous manner. The fraction of diffusing species reads in this case of loading for the plate

$$\tilde{n}(p) = \frac{1}{l\rho_s}\int_0^l\left(\frac{\rho_s}{p} - \tilde{\rho}(x, p)\right)dx \tag{17}$$

yielding in analogy to Eq. (14a):

$$\tilde{n}(p) = \frac{1}{p} - \frac{\alpha l}{D}\frac{\sinh(\beta)}{p\beta(L\cosh(\beta) + \beta\sinh(\beta))}. \tag{18}$$

After Taylor expansion, as mean loading time

$$\overline{\tau} = \tilde{n}(p = 0) = \frac{l^2}{3D} + \frac{l}{\alpha} \tag{19}$$

the same expression as for unloading is obtained (see Eq. (16a).

2.2.2 Determination of mean unloading time from solution $\rho(x, t)$, $\rho(r, t)$

The mean unloading time can also be determined from the solutions $\rho(x, t)$, $\rho(r, t)$ Eq. (6). The number of diffusing species dN_s/dt leaving per time interval dt the plate per area (a), the cylinder per length (b), or the sphere (c) reads

$$\frac{dN_s}{dt} = D\frac{\partial\rho}{\partial x}\Big|_{x=l} = \alpha(\rho_s - \rho(l)), \tag{20a}$$

$$\frac{dN_s}{dt} = 2\pi r_0 D\frac{\partial\rho}{\partial r}\Big|_{r=r_0} = 2\pi r_0\alpha(\rho_s - \rho(r_0)), \tag{20b}$$

$$\frac{dN_s}{dt} = 4\pi r_0^2 D\frac{\partial\rho}{\partial r}\Big|_{r=r_0} = 4\pi r_0^2\alpha(\rho_s - \rho(r_0)). \tag{20c}$$

The mean unloading time is obtained from

$$\overline{\tau} = \frac{1}{N_\infty}\int_0^\infty\left(-\frac{dN_s}{dt}\Big|_{(r=r_0)\text{or}(x=l)}\right)t\,dt \tag{21}$$

with $N_\infty = (\rho_0 - \rho_s)l$ (plate), $N_\infty = \pi r_0^2(\rho_0 - \rho_s)$ (cylinder), $N_\infty = 4\pi r_0^3/3(\rho_0 - \rho_s)$ (sphere). Inserting the solutions Eq. (6) and integrating Eq. (21) yields the mean unloading time for the plate (a), cylinder (b), and the sphere (c):

$$\overline{\tau} = \sum_{n=1}^\infty\frac{2L^2l^2}{D}\frac{1}{\overline{\beta}_n^4(\overline{\beta}_n^2 + L^2 + L)}, \tag{22a}$$

$$\overline{\tau} = \sum_{n=1}^\infty\frac{4L^2r_0^2}{D}\frac{1}{\overline{\beta}_n^4(\overline{\beta}_n^2 + L^2)}, \tag{22b}$$

$$\overline{\tau} = \sum_{n=1}^\infty\frac{6L^2r_0^2}{D}\frac{1}{\overline{\beta}_n^4(\overline{\beta}_n^2 + L(L - 1))}. \tag{22c}$$

with the respective roots according to Eq. (7).

The sums given by Eq. (22) yield identical values for the mean unloading time as the closed-form expressions (Eq. 16). This is verified for selected values of the parameter L making use of the tabulated roots for Eq. (7) given, e.g., in the textbook of Crank [1]. Equating $\overline{\tau}$ according to Eq. (22) with the respective one according to Eq. (16) yields equations with L as single parameter, e.g., for the cylinder

$$\frac{1}{8} + \frac{1}{2L} = \sum_{n=1}^\infty\frac{4L^2}{\overline{\beta}_n^4(\overline{\beta}_n^2 + L^2)}. \tag{23}$$

2.3 Unloading taking into account trapping and detrapping

Next we consider in addition trapping of the diffusing species with a rate σ at homogeneously distributed traps within the sample and detrapping with a rate η from these traps, restricting to a plate-shaped sample. The fraction of trapped species is characterized by the density $\rho_t(t)$ for which the rate equation

$$\frac{d\rho_t}{dt} = \sigma\rho - \eta\rho_t \tag{24}$$

with the corresponding Laplace transform

$$\tilde{\rho}_t = \frac{\sigma}{p+\eta}\tilde{\rho} + \rho_{t,0}\frac{1}{p+\eta} \tag{25}$$

holds with the initial density in traps $\rho_{t,0}$. The diffusion equation for this extended model reads

$$\frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2} - \sigma\rho + \eta\rho_t \tag{26}$$

with the Laplace transform

$$\frac{d^2\tilde{\rho}}{dx^2} - \gamma^2\tilde{\rho} = -\frac{1}{D}\left(\rho_0 + \rho_{t,0}\frac{\eta}{\eta+p}\right) \tag{27}$$

where

$$\gamma^2 = \frac{p(p+\sigma+\eta)}{D(p+\eta)}. \tag{28}$$

We note that the ansatz according to Eqs. (24) and (26) implies that σ is independent of ρ_t, i.e., inexhaustible sink behavior is assumed, meaning that the trap concentration is high compared to ρ_t or else that multiple trapping at a trap site may occur with constant rate.

With the boundary condition Eq. (4a) the following solution is obtained

$$\tilde{\rho}(x,p) = \frac{1}{(p+\sigma+\eta)} \times \left[\alpha\frac{\rho_s(p+\sigma+\eta) - \rho_0(p+\eta) - \rho_{t,0}\eta}{p(D\gamma\sinh(\beta) + \alpha\cosh(\beta))}\cosh(\gamma x)\right.$$
$$\left. + \frac{\rho_0(p+\eta) + \rho_{t,0}\eta}{p}\right] \tag{29}$$

($\beta = \gamma l$) which reduces to Eq. (9a) for $\rho_{t,0} = \eta = \sigma = 0$.

For calculating the mean unloading time, the limiting density in the plate $\rho_s(1+\sigma/\eta)$ after unloading has to be taken into account, leading in extension to Eq. (10a) to

$$\tilde{n}_{ex}(p) = \frac{1}{l(\rho_0 + \rho_{t,0} - \rho_s(1+\frac{\sigma}{\eta}))}$$
$$\int_0^l \left(\tilde{\rho}(x,p) + \tilde{\rho}_t(x,p) - \frac{\rho_s}{p}(1+\frac{\sigma}{\eta})\right)dx. \tag{30}$$

Insertion of $\tilde{\rho}(x,p)$ (Eq. 29) and $\tilde{\rho}_t(x,p)$ Eq. (25) and integration leads to

$$\tilde{n}_{ex}(p) = \frac{1}{(\rho_0 + \rho_{t,0} - \rho_s(1+\frac{\sigma}{\eta}))(p+\eta)} \times$$
$$\left[\alpha\frac{\rho_s(p+\sigma+\eta) - \rho_0(p+\eta) - \rho_{t,0}\eta}{p(D\gamma\sinh(\beta) + \alpha\cosh(\beta))}\frac{\sinh(\beta)}{\beta} + \frac{(\rho_0 + \rho_{t,0} - \rho_s(1+\frac{\sigma}{\eta}))(p+\eta)}{p}\right] \tag{31}$$

Taylor expansion of $\sinh(\beta)$ and $\cosh(\beta)$ yields the mean time of unloading from $\rho_0 + \rho_{t,0}$ down to $\rho_s(1+\sigma/\eta)$:

$$\bar{\tau} = \tilde{n}_{ex}(p=0) = \left(\frac{1}{\eta}\right)\frac{\rho_{t,0} - \rho_s\frac{\sigma}{\eta}}{\rho_0 + \rho_{t,0} - \rho_s(1+\frac{\sigma}{\eta})} + \left(\frac{l^2}{3D}\right.$$
$$\left. + \frac{l}{\alpha}\right)(1+\frac{\sigma}{\eta}). \tag{32}$$

The special case of detrapping exclusively, i.e., $\sigma = 0$, reads

$$\bar{\tau} = \left(\frac{1}{\eta}\right)\frac{\rho_{t,0}}{\rho_0 + \rho_{t,0} - \rho_s} + \left(\frac{l^2}{3D} + \frac{l}{\alpha}\right), \tag{33}$$

which includes as further special case for $\rho_{t,0} = 0$ the solution (Eq. 16a) quoted above. Another special case pertains to vanishing concentration in the surrounding ($\rho_s = 0$):

$$\bar{\tau} = \left(\frac{1}{\eta}\right)\frac{\rho_{t,0}}{\rho_0 + \rho_{t,0}} + \left(\frac{l^2}{3D} + \frac{l}{\alpha}\right)\left(1+\frac{\sigma}{\eta}\right). \tag{34}$$

The determination of the mean unloading time from the solution $\rho(x,t)$ as done in Sect. 2.2.2 is a bit more laborious here. We restrict to the special case of exclusive detrapping ($\sigma = 0$) and vanishing concentration in the surrounding ($\rho_s = 0$) which leads to

$$\bar{\tau} = \frac{1}{1+R}\left\{\sum_{n=1}^{\infty}\frac{2L^2l^2\left[\frac{D\bar{\beta}_n^2}{l^2} - \eta(1+R)\right]}{D\bar{\beta}_n^4\left(\frac{D\bar{\beta}_n^2}{l^2} - \eta\right)\left(\bar{\beta}_n^2 + L^2 + L\right)} + \frac{R\alpha}{l\eta^2}\left[\frac{1}{1 - \frac{1}{L}\bar{q}l\tan(\bar{q}l)} - 1\right]\right\} \tag{35}$$

with

$$R = \frac{\rho_{t,0}}{\rho_0}, \tag{36}$$

$$\bar{q} = \sqrt{\frac{\eta}{D}}, \tag{37}$$

L according to Eq. (8a) and the roots $\bar{\beta}_n$ according to Eq. (7a). The derivation of Eq. (35) is outlined in the appendix.

The solution Eq. (35) reduces to Eq. (22a) for the special case of $R = 0$, i.e., $\rho_{t,0} = 0$. Again it can be verified for given

data sets that Eq. (35) yields identical values for the mean unloading time as the closed-form expression (Eq. 33).

3 Discussion and conclusion

The main objective of this work lays on the closed-form expressions for the mean time $\overline{\tau}$ of unloading Eq. (16) and loading Eq. (19) for various geometries (plate, cylinder, sphere) and the extension to concomitant trapping and detrapping Eqs. (32), (33) and (34). These closed-form expressions for $\overline{\tau}$ are derived in a straight-forward manner from the Laplace transform $\tilde{n}(p)$ Eq. (11) at $p = 0$, avoiding their calculation by means of sums Eqs. (22) and (35) for which roots Eq. (7) have to be determined.

On the same concept used here to deduce a mean value (Eq. 12) from a Laplace transform for $p \to 0$ (Eq. 13) also the mean action time [15], the mean residence time [17], or the mean-first-passage time [18] is based. In fact, it can be shown that the mean value according to Eq. (13) also follows by applying the relation for the first moment considered in references [17] and [18] $[\int_0^\infty -t f(t) \mathrm{d}t = -\lim_{p\to 0}(\mathrm{d}/\mathrm{d}p)f\tilde{(}p)]$.

The rate-limiting processes in the considered diffusion model is, on the one hand, the diffusion characterized by D Eq. (2), and, on the other hand, the rate constant α Eq. (4), describing the surface reaction. Both rate-limiting processes contribute to the mean times of unloading and loading Eqs. (16) and (19). A relation analogous to that of the mean time for the one-dimensional case Eq. (16a) is reported for the mean residence time of percutaneous drug absorption [17]. Also from a consideration of the mean action time, sum terms of type l^2/D and l/α are found for the characteristic time constant [15].

For obvious reason, $\overline{\tau}$ increases both with decreasing diffusivity and reactivity. The solutions contain the two limiting cases, namely,

- The entirely diffusion-controlled process where the surface acts as ideal sink (i.e., $\alpha \to \infty$), and
- The entirely reaction-controlled process for $D \to \infty$.

Since the reaction-limitation $1/\alpha$ of $\overline{\tau}$ scales linearly with the size (l, r_0) of the object, whereas the diffusion-limitation $(1/D)$ with the square of the size (l^2, r_0^2), for decreasing object size reaction-limitation gets more relevant compared to diffusion-limitation and vice versa for increasing object size.

For a quantitative comparison of the contributions for $\overline{\tau}$ arising from diffusion- (l^2/D) and rate-limitation (l/α), we consider one example of materials science (i) and one of biology (ii):

(i) For electrochemically induced hydrogen transport through an amorphous Pd-rich alloy, the values $D = 1.6 \times 10^{-8}$ cm^2/s and $\alpha = 2.3 \times 10^{-4}$ cm/s are reported [19].[1] For the one-dimensional case, reaction-limitation exceeds diffusion-limitation for a layer thickness l smaller than about 2 μm, and vice versa.

(ii) For oxygen uptake in a spherical cell, the values $D = 1.6 \times 10^{-5}$ cm^2/s and $\alpha = 2 \times 10^{-2}$ cm/s are quoted [20]. From Eq. (16c), a cell radius $r_0 = 5 \times 10^{-3}$ cm is obtained for which reaction- and diffusion-limitation contribute in equal amount.

For comparison of $\overline{\tau}$ for plate, cylinder, and sphere, one may consider $\overline{\tau}l^2/D$ (plate), respectively $\overline{\tau}r_0^2/D$ (cylinder, sphere), yielding from Eq. (16)

$$\left(\frac{1}{3} + \frac{1}{L}\right)\Big|_{\text{plate}} > \left(\frac{1}{8} + \frac{1}{2L}\right)\Big|_{\text{cylinder}} > \left(\frac{1}{15} + \frac{1}{3L}\right)\Big|_{\text{sphere}}$$

(38)

with L according to Eq. (8). The comparison Eq. (38) shows that the mean unloading time is highest for the plate and shortest for the sphere. This reflects the decreasing mean diffusion length for reaching the surface when going from planar to cylindrical and further to spherical symmetry. Related to identical L-values, diffusion-limitation is stronger for a plate than for a sphere; this becomes also evident from the ratio of the diffusion-limited first summand and the reaction-limited second summand of $\overline{\tau}$ Eq. (16), which is $L/3$, $L/4$, and $L/5$ for plate, cylinder and sphere, respectively.

It is worthwhile to mention that the mean time for unloading Eq. (16) does neither depend on the initial concentration ρ_0 nor on the concentration ρ_s in the surrounding. As evident from the solution Eq. (6), ρ_0 and ρ_s affect the magnitude of $\rho(x, t)$ or $\rho(r, t)$, but not their temporal evolution.

For unloading with concomitant trapping and detrapping, the following conclusions can be drawn with respect to the mean unloading time:

- $\sigma = 0, \rho_s > 0$, Eq. (33): Release of trapped species by detrapping with a rate η increases the time $\overline{\tau}$ needed for unloading. The first summand in Eq. (33) describes the mean time $1/\eta$ of release from traps weighted by the density of species ρ_t being trapped initially related to the density $(\rho_0 + \rho_{t,0} - \rho_s)$ being unloaded. The second term, which corresponds to the solution without detrapping Eq. (16a), describes the mean time for diffusion- and reaction-limited outdiffusion.

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[1] The rate constant α corresponds to $k_1/c_{\max}$ quoted in the cited reference.

- $\sigma > 0, \rho_s = 0$, Eq. (34): Additional trapping with a rate σ further increases the time for unloading. Intermediate trapping with subsequent detrapping slows down the out-diffusion; this is the reason why the $\overline{\tau}$-increase is determined by the ratio σ/η of trapping and detrapping rate.

- General case ($\sigma > 0, \rho_s > 0$), Eq. (32): For non-vanishing concentration in the surrounding ($\rho_s > 0$, Eq. (32), the weighting factor of the first summand ($1/\eta$) is modified compared to Eq. (33). The factor $(\rho_{t,0} - \rho_s\sigma/\eta)$ $/(\rho_0 + \rho_{t,0} - \rho_s(1 + \sigma/\eta))$ takes into account that for $\rho_s > 0$, the part of species released from the traps is reduced by $\rho_s\sigma/\eta$ and the part of species, which is unloaded by diffusion to the surface, is reduced by $\rho_s(1 + \sigma/\eta)$.

For $\sigma > 0$, the mean time $\overline{\tau}$ is essentially determined by the ratio σ/η of trapping and detrapping rates Eqs. (32) and (34). For a quantitative assessment of this ratio, we consider an example of hydrogen trapping at dislocations in steel [21, 22]. For a low occupancy of trap sites by hydrogen, as underlying the present model, the ratio σ/η can be written as $\sigma/\eta = N_t/N_l \exp(-E_T/k_B T)$, where N_t, N_l denotes the trap and lattice site density, respectively, and E_T the binding energy of hydrogen at dislocations.[2] For $N_t = 2 \times 10^{21}$ 1/m^3, corresponding to a dislocation density of 10^{12} 1/m^2, $N_l = 5.1 \times 10^{29}$ 1/m^3, and $E_T = -60$ kJ/mol (values from [21]), a ratio $\sigma/\eta = 195$ follows for ambient temperature (293 K). This high value reflects the fact that due to thermally activated process of detrapping, the detrapping rate may be much lower than the trapping rate. As evident from Eqs. (32) and (34), a sluggish detrapping may give rise to a strong increase of the mean unloading time (factor $(1 + \sigma/\eta)$ in Eqs. (32) and (34). The slowing down of the diffusion process by trapping is in literature also described by means of a reduced effective diffusivity D_{eff} in comparison to D. It is worthwhile to mention that the ratio between D_{eff} and D in the above mentioned case is given by inverse of the same factor $(1 + \sigma/\eta)$ (see [21]).

In conclusion, comparing the two approaches for calculating the mean unloading/loading time, i.e., by means of the Laplace transform Eq. (11) at $p = 0$ or via Eq. (21) by means of $\rho(x, t)$ or $\rho(r, t)$, the advantage of the first one becomes evident, even for the simple model presented in this work, and most clearly for the complexer model including detrapping. When with increasing complexity the calculation of $\rho(x, t)$ ($\rho(r, t)$) from the inverse of the Laplace transform $\tilde{\rho}(x, p)$ ($\tilde{\rho}(r, p)$) becomes more and more laborious, the determination of mean values from $\tilde{n}(p)$ pays off as a most direct and simple way. Above all, in contrast to sum-type solutions the closed-form expressions enable in a straightforward manner physical insight in the mean loading or unloading time

and its relation to the various controlling parameters, such as D, α, or ρ_s.

Appendix: Derivation of Eq. (35)

For exclusive detrapping (i.e., $\sigma = 0$) the solution Eq. (29) reduces to

$$\tilde{\rho}(x,p) = \frac{1}{(p+\eta)}\left[\alpha\frac{(\rho_s - \rho_0)(p+\eta) - \rho_{t,0}\eta}{p(D\gamma\sinh(\beta) + \alpha\cosh(\beta))}\cosh(\gamma x)\right.$$
$$\left. + \frac{\rho_0(p+\eta) + \rho_{t,0}\eta}{p}\right]$$

(A-1)

with

$$\gamma^2 = \frac{p}{D}$$

(A-2)

according to Eq. (28) and $\beta = \gamma l$.

Determination of the solution, i.e., the inverse $\rho(x, t)$ of the Laplace transform $\tilde{\rho}(x, p)$ requires the calculation of the numerator $f(p)$ and the derivative $dg(p)/dp$ of the denominator $g(p)$ of Eq. (A-1) at the roots of $g(p)$ [1]. Roots of the denominator $g(p) = p(p+\eta)(D\gamma\sinh(\beta) + \alpha\cosh(\beta))$ of Eq. (A-1) are (i) $p = 0$, (ii) $\alpha\cosh(ql) + Dq\sinh(ql) = 0$, and (iii) $p = -\eta$, where the second one corresponds to Eq. (7a) ($\overline{\beta}_n \tan\overline{\beta}_n = L$).

The derivative of $dg(p)/dp$ reads with $d\gamma/dp = 1/(2D\gamma)$

$$g'(p) = \cosh(\beta)\left[\alpha(2p+\eta) + \frac{lp(p+\eta)}{2}\right]$$
$$+ \sinh(\beta)\left[D\gamma(2p+\eta) + \frac{p(p+\eta)}{2\gamma}(L+1)\right]$$

(A-3)

- For root (i) the demoninator derivative is

$$g'(0) = \alpha\eta$$

(A-4)

  and the numerator $f(p)$ of Eq. (A-1)

$$f(0) = \alpha\eta\rho_s .$$

(A-5)

- For root (ii) one obtains

$$g'(\overline{\beta}_n) = \cos\overline{\beta}_n\left(\frac{D\overline{\beta}_n^2}{l^2} - \eta\right)\frac{D}{2l}(\overline{\beta}_n^2 + L^2 + L)$$

(A-6)

  for the derivative Eq. (A-3) with $\beta_n^2 = -\overline{\beta}_n^2$ and

$$f(\overline{\beta}_n) = \alpha\left[(\rho_s - \rho_0 - \rho_{t,0})\eta - (\rho_s - \rho_0)\frac{D\overline{\beta}_n^2}{l^2}\right]\cos\left(\frac{\overline{\beta}_n x}{l}\right)$$

(A-7)

  for the numerator.

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[2] Follows from Eq. (20a) of [21].

- For root (iii) the derivative reads

$$g'(-\eta) = \eta\left(-\alpha\cos(\overline{q}l) + D\overline{q}\sin(\overline{q}l)\right) \tag{A-8}$$

with $\overline{q} = \sqrt{\eta/D}$ (Eq. 37) and the numerator

$$f(-\eta) = \eta\rho_{t,0}\left(-\alpha\cos(\overline{q}x) + \alpha\cos(\overline{q}l) - D\overline{q}\sin(\overline{q}l)\right). \tag{A-9}$$

The inverse $\rho(x,t)$ of the Laplace transform $\tilde{\rho}(x,p)$ therefore reads

$$\rho(x,t) = \rho_s +$$

$$\sum_{n=1}^{\infty} \frac{2L\left[(\rho_s - \rho_0 - \rho_{t,0})\eta - (\rho_s - \rho_0)\frac{D\overline{\beta}_n^2}{l^2}\right]\cos\left(\frac{\overline{\beta}_n x}{l}\right)}{\cos\overline{\beta}_n\left(\frac{D\overline{\beta}_n^2}{l^2} - \eta\right)\left(\overline{\beta}_n^2 + L^2 + L\right)}\exp\left(-\frac{D\overline{\beta}_n^2}{l^2}t\right) +$$

$$\rho_{t,0}\left[\frac{\cos(\overline{q}x)}{\cos(\overline{q}l) - \frac{1}{L}\overline{q}l\sin(\overline{q}l)} - 1\right]\exp(-\eta t) \tag{A-10}$$

with $\overline{q} = \sqrt{\eta/D}$ Eq. (37) and $\overline{\beta}_n\tan\overline{\beta}_n = L$ Eq. (7a). For $\eta = 0$ and $\rho_{t,0} = 0$ the solution without traps (Eq. 6a) is obtained.

The mean unloading time $\overline{\tau}$ is obtained from the solution Eq. (A-10) by means of Eq. (21) with

$$\frac{dN_s}{dt} = \alpha(\rho_s - \rho(l)) \tag{A-11}$$

and with $N_\infty = (\rho_0 + \rho_{t,0} - \rho_s(1 + \sigma/\eta))l$. Restricting to the case of vanishing concentration in the surrounding ($\rho_s = 0$) leads to the result Eq. (35) given in Sect. 2.3.

The second denominator of Eq. (35) gets 0 if $(\overline{q}l\tan(\overline{q}l) = L)$ holds for the values $\overline{q} = \sqrt{\eta/D}$. For this special ratio of η and D also the factor $\left(D\overline{\beta}_n^2/l^2 - \eta\right)$ of the first denominator gets 0 taking into account the condition for the poles $(\overline{\beta}_n\tan\overline{\beta}_n = L)$ of the sum.

Declarations

Conflict of interest None.

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