Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.770273

51 (2013) 4343–4349
June

Derivation of the permeation equation for diffusion of gases and vapors in flat membrane by using Laplace transform

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Received 27 March 2012; Accepted 16 November 2012

ABSTRACT

Generally, the model of forced diffusion of a penetrant through nonporous polymer membranes can be quantitatively described by a partial differential equation of parabolic type, which is known as Fick's second law. In this article, the detailed explanation of application of the integral transform method (especially Laplace transform) for the solution of Fick's second law at given initial and boundary conditions is presented. Obtained final expression for the concentration profile inside a flat membrane and the diffusion flux through a membrane were verified on permeability data of carbon dioxide and cyclohexane through low-density polyethylene membrane. While CO_2 permeation data can be successfully fitted by obtained model, in the case of cyclohexane vapors, when the diffusion coefficient cannot be supposed to be constant due to strong polymer–penetrant interactions (swelling), the agreement between model and experimental data is lower.

Keywords: Laplace transform; Diffusion; Gas/vapor permeation; Flat membrane

1. Introduction

The mass transport through polymer membranes caused by the gradient of concentration is a complex process, which depends on the nature of the membrane and the penetrating substance as well. In isotropic, nonporous polymer membranes the transport mechanism can be described by the solution–diffusion model [1], which can be considered as a sequence of consecutive processes of sorption, activated diffusion and desorption. The model is characterized by permeability, diffusion and sorption coefficients [2].

Usually, two methods are used for the determination of diffusion coefficients by solving of Fick's second law at given initial and boundary conditions. The first method is the separation of variables (solution is in the form of Fourier series), the second one is the Laplace transform. The solution of Fick's second law by the method of the separation of variables is in detail described in the literature [3] in contrast to the solution of this diffusion equation by Laplace transform. Crank published [3 chapter 4, page 52] the relation for dependence of the diffusion flux on initial concentration, diffusion coefficient, time and membrane thickness only, without the derivation of this

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relation. He referred to the paper of Rogers et al. [4], where is also only the reference to work of Courant and Hilbert [5] and to Holsteins Westinghouse Research Report. In fact Holstein applied the transformation formula

$$\varphi(x) = \frac{1}{\sqrt{x}} \quad \varphi\left(\frac{1}{x}\right) \tag{1}$$

where

$$\varphi(x) = \sum_{\mu=-\infty}^{\infty} e^{-\pi\mu^2 x} \tag{2}$$

which validity was proved on the mentioned book [5], to the relation for diffusion flux in the form of Fourier series only. Thus, to our best knowledge, no detailed explanation of application of Laplace transform for solving of diffusion equations has been published yet.

Therefore, in this work, we present a novel approach with application of Laplace transform on Fick's second law in order to obtain the relation for concentration profile in the membrane and for diffusion flux through the flat polymer membrane at given initial and boundary conditions.

Illustration and verification of presented Laplace transform based diffusion model was done using carbon dioxide—Low-density polyethylene membrane (LDPE) and cyclohexane—LDPE systems.

2. Laplace transform

Referring to the definition of Laplace transform and some results following from this theory [6], the real function of two variables $c(x,t)$ describing the dependence of concentration on coordinate and time is considered. Variable x is understood as a parameter. Further, the integral of the real function (Eq. (3)) has to exists and has finite value at least for some complex number. Then, the function $M(x,p)$ can be defined by the relation

$$L\{c(x,t)\} = M(x,p) = \int_0^{\infty} c(x,t)\, e^{-pt} dt. \tag{3}$$

Obtained Laplace transform pair consists of the original function $c(x,t)$ and the transform function with two variables $M(x,p)$.

The real function $c(x,t)$ must fulfill several requirements. The first of them is a piecewise continuity in the interval $t \in \langle 0, \infty)$. This is satisfied if the function is piecewise continuous in all intervals $t \in \langle 0, a \rangle$, where a is an arbitrary positive number. In other words, the function $c(x,t)$ has to be continuous in this finitely many intervals except in points with first order discontinuity. A point of first-order discontinuity if the function is discontinuous in this point and it has finite one sided limits in this point. This property can be used if the real function $c(x,t)$ exhibits sharp changes.

Next, requirement is that the real function $c(x,t)$ has to be of exponential order with index of increase ξ_0. This holds only if the point $+\infty$ is an accumulation point of the domain of the real function $c(x,t)$ and if there exists such t_0 and such number $K>0$ that the inequality $|c(x,t)| \leqslant K e^{\xi_0 t}$ holds for all $t>t_0$ for which the real function $c(x,t)$ is defined. Further, for all $t<0$, the real function $c(x,t)$ is equal to zero.

If the real function $c(x,t)$ satisfies all above-mentioned conditions, the following theorem can be established. If $c(x,t)$ is continuous and $\partial c(x,t)/\partial t$ is piecewise continuous and if both functions of variable t, then we can state

$$L\left\{\frac{\partial c(x,t)}{\partial t}\right\} = p\, L\{c(x,t)\} - c(x,0+), \tag{4}$$

where $c(x,0+) = \lim\limits_{t \to 0+} c(x,t)$ is the initial value of $c(x,t)$.

However, the diffusion equations still contain derivatives with respect to x coordinate in the definition of the Laplace transform (3).

Theorem 1 *Let $c(x,t)$ and $\partial c(x,t)/\partial t$ are continuous functions of variables x, t for $x \in \langle 0, l \rangle$ and $t \geqslant 0$ and next let constants K, ξ_0 satisfy*

$$|c(x,t)| \leqslant K e^{\xi_0 t}, \ |\partial c/\partial x| \leqslant K e^{\xi_0 t} \tag{5}$$

for all $x \in \langle 0, l \rangle$ and $t \geqslant 0$. Then

$$L\left\{\frac{\partial c(x,t)}{\partial x}\right\} = \frac{dM(x,p)}{dx} \tag{6}$$

holds for $x \in \langle 0, l \rangle$, $\mathrm{Re}\, p > \xi_0$.

This relation can be generalized for derivatives of higher order with respect to x and also holds at the boundary points of the interval.

It is necessary to emphasize that the above-mentioned theorem requires the continuity of the real function $c(x,t)$. Thus, if the real function $c(x,t)$ contains discontinuities of the first order, then the diffusion problem must be separated to identical quantity to the number of appropriate discontinuities. Alternatively, such problem can be solved using the generalized inverse Laplace transform. Contrary to our proposed method, where diffusion problem is formulated for the diffusion of gases or vapors in a polymeric membrane and the points of first order discontinuity did not occur, such problem therefore was not considered.

3. Transform of diffusion problem

The diffusion problem can be formulated as:

$$\begin{aligned} &\tfrac{\partial c}{\partial t} = D\tfrac{\partial^2 c}{\partial x^2} \\ &c(0,t) = c_0 \\ &c(l,t) = 0 \\ &c(x,0) = 0, \quad x \in \langle 0, l \rangle \end{aligned} \tag{7}$$

Thus, Laplace transform of the function obtained by using relation (4) can be expressed by

$$L\left\{\frac{\partial c(x,t)}{\partial t}\right\} = p\,M(x,p). \tag{8}$$

and Laplace transform of the function $\partial^2 c(x,t)/\partial x^2$ using Theorem 1 can be expressed by:

$$L\left\{\frac{\partial^2 c(x,t)}{\partial x^2}\right\} = \frac{d^2 M(x,p)}{dx^2} \tag{9}$$

Substitution of Eqs. (8) and (9) into the diffusion problem (7) leads to the ordinary differential equation of the second order for the complex function of the real variable:

$$\frac{d^2 M(x,p)}{dx^2} - \frac{p}{D} M(x,p) = 0 \tag{10}$$

The boundary conditions following from the diffusion problem (7) can be defined as:

$$\begin{aligned} &M(0,p) = \textstyle\int_0^\infty c_0 e^{-pt} dt = \tfrac{c_0}{p} \\ &\lim_{x \to l} M(x,p) = 0 \end{aligned} \tag{11}$$

The general solution of the differential Eq. (10) is given in the form

$$M(x,p) = A_1(p) e^{\sqrt{\frac{p}{D}}x} + A_2(p) e^{-\sqrt{\frac{p}{D}}x}. \tag{12}$$

where with respect to appropriate boundary conditions, following set of two algebraic equations is obtained

$$\begin{aligned} &\tfrac{c_0}{p} = A_1(p) + A_2(p) \\ &0 = A_1(p) e^{\sqrt{\frac{p}{D}}l} + A_2(p) e^{-\sqrt{\frac{p}{D}}l} \end{aligned} \tag{13}$$

After finding of $A_1(p)$ and $A_2(p)$ we get particular solution in the form

$$M(x,p) = \frac{c_0}{p}\left[\frac{e^{\sqrt{\frac{p}{D}}x}}{1 - e^{2l\sqrt{\frac{p}{D}}}} + \frac{e^{-\sqrt{\frac{p}{D}}x}}{1 - e^{-2l\sqrt{\frac{p}{D}}}}\right] \tag{14}$$

whereas for the individual parts of the Eq. (14), we can write

$$M_1(x,p) = \frac{c_0\, e^{\sqrt{\frac{p}{D}}x}}{p\left(1 - e^{2l\sqrt{\frac{p}{D}}}\right)} \tag{15}$$

$$M_2(x,p) = \frac{c_0\, e^{-\sqrt{\frac{p}{D}}x}}{p\left(1 - e^{-2l\sqrt{\frac{p}{D}}}\right)} \tag{16}$$

If Eq. (15) is multiplied by expression $e^{-2l\sqrt{\frac{p}{D}}}/e^{-2l\sqrt{\frac{p}{D}}}$ and rearranged, we obtain for $M_1(x,t)$ expression in form:

$$M_1(x,p) = -\frac{c_0\, e^{(x-2l)\sqrt{\frac{p}{D}}}}{p\left(1 - e^{-2l\sqrt{\frac{p}{D}}}\right)} \tag{17}$$

With respect to the formula for the sum of geometric series

$$\sum_{n=0}^{\infty} y^n = \frac{1}{1-y}, \quad |y|<1 \tag{18}$$

Eqs. (15) and (16) can be expressed in following form as

$$\begin{aligned} &M_1(x,p) = -\tfrac{c_0}{p} \textstyle\sum_{n=0}^{\infty} e^{(x-2l)\sqrt{\frac{p}{D}}} e^{(-2nl)\sqrt{\frac{p}{D}}} \\ &M_1(x,p) = -\tfrac{c_0}{p} \textstyle\sum_{n=0}^{\infty} e^{-2l(n+1)-x\sqrt{\frac{p}{D}}} \end{aligned} \tag{19}$$

$$M_2(x,p) = \frac{c_0}{p} \sum_{n=0}^{\infty} e^{-(2n1+x)\sqrt{\frac{p}{D}}} \tag{20}$$

and the solution expressed by Eq. (14) can be rewritten in the form

$$M(x,p) = \frac{c_0}{p} \sum_{n=0}^{\infty} \left[-e^{-(2l(n+1)-x)\sqrt{\frac{p}{D}}} + e^{(-2nl+x)\sqrt{\frac{p}{D}}}\right], \tag{21}$$

Solution over the set of complex numbers is only a first part of the problem. After that, such solution has to be transformed to the set of real numbers. Procedure that is necessary for such purpose will be described in following part.

4. Concentration profile and diffusion flux

In order to find the whole Laplace transform pair, following three assumptions must be fulfilled:

(i) Regularity of the function $M(x,p)$ in the half-plane $\mathrm{Re}\, p>\xi$.

(ii) Existence of a sequence of circles centered at the point $p=0$ whose radius increases to infinity. If we denote A_n as the maximum of the module $M(x,p)$ on the part of the *n-th* circle pertaining to the half-plane $\mathrm{Re}p \geqslant \xi_0>\xi$, then $\lim\limits_{n\to\infty} A_n = 0$.

(iii) Convergence of the integral $\int_{a-i\infty}^{a+i\infty} |M(x,p)|dp$.

If the transforming function $M(x,p)$ satisfies these assumptions, the original function exists and has a form

$$c(x,t) = \frac{1}{2\pi\, i}\int_{\xi_0-i\infty}^{\xi_0+i\infty} M(x,p)\, e^{pt} dp \tag{22}$$

and is continuous of exponential order with index of increase ξ_0. Further, Eq. (22) equals to zero for $t \leqslant 0$ and satisfies the condition of equality $c(x,t) = L^{-1}\{M(x,p)\}$. For simplicity, a relation (21) will be written in the form $M(x,p) = \sum_{n=0}^{\infty} M_n(x,p)$.

If function $M_n(x,p)$ satisfies all three foregoing assumptions (i)–(iii) and the series $\sum_{n=0}^{\infty} M_n(x,p)$ converges uniformly for $p \in [0,P]$ for each finite $p>0$, then the function $G(x,p)$, defined as $G(x,p) = \sum_{n=0}^{\infty} |M_n(x,p)|$, satisfies these three assumptions as well. If a parameter ξ_0 is the common index of increase for all functions $M(x,p)$ and the function $G(x,p)$, then for $\mathrm{Re}p>\xi_0$ we obtain the following relation

$$L^{-1}\left\{\sum_{n=0}^{\infty} M_n(x,p)\right\} = \sum_{n=0}^{\infty} L^{-1}\{M_n(x,p)\}. \tag{23}$$

Furthermore, Laplace transform of the distribution function is known [7] and defined as

$$L\left\{\frac{1}{\sqrt{\pi t}}\, e^{-\frac{z^2}{4t}}\right\} = \frac{1}{\sqrt{p}} e^{-z\sqrt{p}}, \quad z>0 \tag{24}$$

and the error function is defined by an integral

$$\mathrm{erf}\,(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-u^2} du, \tag{25}$$

which can be rewritten to the form

$$\mathrm{erf}\left(\frac{z}{2\sqrt{t}}\right) = \int_0^z \frac{1}{\sqrt{\pi t}}\, e^{-\frac{r^2}{4t}} dr, \tag{26}$$

where the substitution $u = \frac{r}{2\sqrt{t}}$ was done.

Integrating of Eq. (24) over z using Eq. (26) leads to expression

$$L\left\{\int_0^z \frac{1}{\sqrt{\pi t}}\, e^{-\frac{r^2}{4t}} dr\right\} = \int_0^z \frac{1}{\sqrt{p}} e^{-r\sqrt{p}} dr \tag{27}$$

and consequently to the following transform pair expressed as

$$L\left\{\mathrm{erf}\left(\frac{z}{2\sqrt{t}}\right)\right\} = \frac{1}{p} - \frac{1}{p} e^{-z\sqrt{p}}, \quad z>0. \tag{28}$$

By a simple modification of (28) can be obtained for transform pair expression

$$L\left\{\mathrm{erfc}\left(\frac{z}{2\sqrt{t}}\right)\right\} = \frac{1}{p} e^{-z\sqrt{p}}, \quad z>0. \tag{29}$$

With respect to Eq. (21) and to condition in Eq. (29), two following expressions can be obtained

$$\frac{x+2nl}{\sqrt{D}}>0 \quad \text{and} \quad \frac{2l(n+1)-x}{\sqrt{D}}>0 \tag{30}$$

which satisfy the physical point of view. Applying relations (23) and (29) onto Eq. (21), the expression for concentration profile of two variables (*x*,*t*) can be obtained

$$c(x,t) = c_0 \times \sum_{n=0}^{\infty}\left[-\mathrm{erfc}\left(\frac{2l(n+1)-x}{2\sqrt{Dt}}\right) + \mathrm{erfc}\left(\frac{x+2nl}{2\sqrt{Dt}}\right)\right]. \tag{31}$$

Combination of Eq. (31) with the Ficks first law, we can write for the diffusion flux

$$j(x,t) = c_0\sqrt{\frac{D}{\pi\, t}} \times \sum_{n=0}^{\infty}\left[e^{-\frac{(2l(n+1)-x)^2}{4Dt}} + e^{-\frac{(x+2nl)^2}{4Dt}}\right]. \tag{32}$$

In the case of transport of medium (gas and vapor) through the isotropic flat membrane with the thickness *l*, the diffusion flux expressed by (32) can be rewritten to

$$j(l,t) = 2c_0\sqrt{\frac{D}{\pi\ t}}\sum_{n=0}^{\infty} e^{-\frac{(2n+1)^2 l^2}{4Dt}}. \tag{33}$$

This relation is important not only for determination of the diffusion coefficient but also for determination of the permeability coefficient as transport parameter defined at the steady state when the gradient of concentration is constant.

5. Application of model on the experimental data

The verification of derived final diffusion relation was made by fitting of theoretical diffusion curves for carbon dioxide and cyclohexane in flat LDPE on the experimental data obtained by differential permeation method [8] at initial and boundary conditions, which corresponded with relation (7).

5.1. Materials

Low-density polyethylene membrane BRALEN FB2–30 (LDPE) was supplied by Slovnaft Company (Slovakia). The thickness of antistatic membrane sample was $(50 \pm 1) \times 10^{-6}\,\mathrm{m}$. The degree of crystallinity was reported to be 45%, and the density determined by mercurial pycnometry was $\rho = 919 \pm 2\,\mathrm{kg\,m^{-3}}$ at 25°C [8,12].

Cyclohexane (p.a. grade from Sigma-Aldrich) was used without further purification, and carbon dioxide (purity at least 99.99%) was purchased from Linde and used as received.

5.2. Permeation experiment

Permeation experiments of carbon dioxide and cyclohexane were carried out at 25°C and at selected pressures using home-built differential flow permeameter with hydrogen as a carrier gas according to the procedure described in detail in the literature [8]. Obtained experimental data were analyzed by the normalized diffusion curves. The diffusion flux at the steady state as the limit $\lim_{t\to\infty} j(l,t)$ is given by using transformation formula (1) on diffusion relation (33)

$$j_s = \frac{Dc_0}{l}. \tag{34}$$

The relation for normalized diffusion flux is given by combination of formulas (33) and (34)

$$j_N(l,t) = \frac{2l}{\sqrt{\pi D t}}\sum_{n=0}^{\infty} e^{-\frac{(2n+1)^2 l^2}{4Dt}}. \tag{35}$$

Relation (35) was used for the calculation of diffusion coefficient of carbon dioxide in LDPE membrane. The dependence of theoretical and experimental normalized fluxes of carbon dioxide through LDPE membrane on time is presented by Fig. 1. The concentration profile of carbon dioxide inside the membrane, it means the dependence of concentration of carbon dioxide on position and time, is shown on Fig. 2. Concentration profile in LDPE membrane was predicted on base of relationship (31) and confirmed initial and boundary conditions (7).

It can be seem from both the figures very good agreement between experimental points and theoretical curve obtained on the base of relation (33). This relation was derived by method of Laplace transform for a constant diffusion coefficient. Obtained value of CO_2 diffusion coefficient using Gauss–Newton optimization method [9] at 25°C is $D(CO_2) = 2.27 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$, which corresponds rather well with the range $(1.5,\ 4.5) \times 10^{-11}\ \mathrm{m^2.s^{-1}}$ obtained by integral method reported in the literature [10,11].

In Fig. 3, we show the dependence of theoretical and experimental normalized fluxes of cyclohexane through LDPE membrane on time also obtained by relation (33) at the temperature of 25°C and at cyclohexane relative vapor activity $a_r = 0.6$, where $a_r = p/p_{\mathrm{sat}}$ and p_{sat} is pressure of saturated vapors 13.07 kPa. The discrepancy between the theoretical curve and experimental points is quite can be seen. This

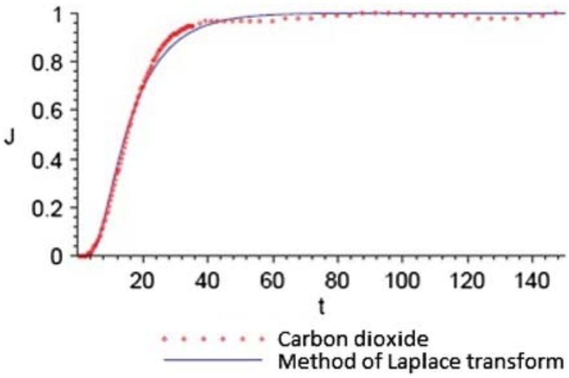

Fig. 1. Correct optimalization of diffusion curve for permeation of carbon dioxide in LDPE: Dependence of diffusion flux *J* ($\mathrm{mol\,m^{-2}\,s^{-1}}$) on time *t* (s).

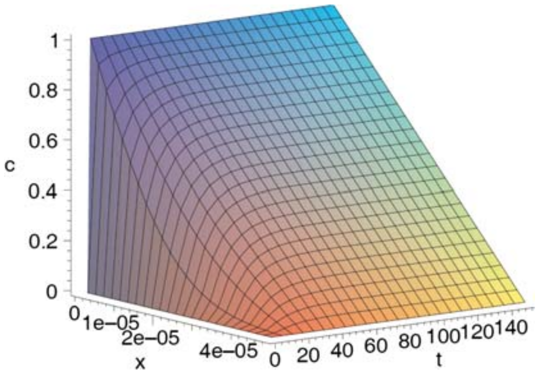

Fig. 2. Prediction of concentration profile for permeation of carbon dioxide in LDPE: Dependence of concentration c (mol m^{-3}) on coordinate x (m) and on time t (s).

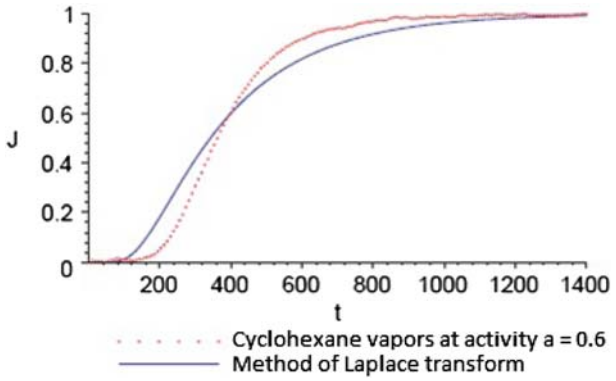

Fig. 3. Incorrect optimalization of diffusion curve for permeation of cyclohexane in LDPE: Dependence of diffusion flux J (mol m^{-2} s^{-1}) on time t (s).

difference is caused by fact that the diffusion coefficient of cyclohexane is not constant in this case and depends on concentration due to swelling of LDPE membrane in contact with cyclohexane vapors [8,12].

6. Conclusions

A novel approach for the application of Laplace transform was used for the solution of Fick's second law at given initial and boundary conditions. Derived relation for concentration profile in membrane is a proof of works published without any deduction earlier by Crank and Holstein those published the concentration profiles obtained by the generally known Fourier method of separation of variables. Contrary to concentration profiles obtained by Laplace transform are more useful because of faster convergence. Derived equation for normalized diffusion flux of penetrant through non-porous membrane allows to evaluate (constant) diffusion coefficient of appropriate medium. For polymer + penetrant systems with low mutual interactions, derived equation can be applied without any limitations. However, application of equation for systems where mutual interactions cannot be neglected (like hydrocarbon vapors in polyethylene) and the diffusion coefficient cannot be supposed as a constant is limited.

Acknowledgements

The financial support of Czech Ministry of Education, Youth and Sports (Grant MSM No.6046137307 and grant MSM 6046137306) and Grant Agency of Czech Republic (P106/10/1194) is gratefully acknowledged.

List of physical symbols

Concentration — C, mol m^{-3}
Diffusion flux — j, mol m^{-2} s^{-1}
Diffusion coefficient — D, m^{2} s^{-1}
Coordinate — x, z, m
Thickness of membrane — l, m
Time — t, s
Density — ρ, kg m^{-3}
Activity — a

List of mathematical symbols

General functions — φ, y
Variables — u, r
Laplace transform — L
Inverse Laplace transform — L^{-1}
Imaginary unit — i
Complex parameters — p
Constant parameters — μ, K
Parametric functions — $A_1(p)$, $A_2(p)$
Complex functions — M, G
Maximum of module — A_n
Index of increase — ξ

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