

In: Rudolph, V.; Keey, R.B., eds. Drying 94: Proceedings of 9th International drying symposium (IDS '94); 1994 August 1-4; Gold Coast, Australia. [Place of publication unknown]: [Publisher unknown]: 141-148. Vol. A.

DERIVATION OF SURFACE EMISSION COEFFICIENT IN ISOTHERMAL DIFFUSION ANALYSES

Jen Y. Liu

U.S. Department of Agriculture, Forest Service
Forest Products Laboratory
Madison, Wisconsin 53705-2398

Keywords: concentration of diffusing substance; desorption; diffusion coefficient; diffusion equation; sorption; surface emission coefficient

ABSTRACT

The movement of a diffusing substance within a medium is controlled by a diffusion coefficient; at the surface of the medium, it is controlled by a surface emission coefficient. The effects of the diffusion and surface emission coefficients must therefore influence the shape of the diffusion curve that describes the variation of the fraction of total concentration of diffusing substance in the medium with time. Earlier, Liu presented an analytical method to separate the diffusion and surface emission coefficients from any experimental diffusion curve using Newman's solutions and Crank's half-time technique. The values of the constant diffusion coefficient in Newman's solutions obtained from a set of properly controlled diffusion curves could be used to derive a variable diffusion coefficient expressed as a function of the concentration of diffusing substance. In this paper, mathematical equations for the surface emission coefficient corresponding to the variable diffusion coefficient are obtained, the variable diffusion coefficient being assumed to be an exponential function of the concentration of diffusing substance. The same diffusion curves used to obtain the variable diffusion coefficient are needed for the evaluation of the surface emission coefficient. However, the variable diffusion coefficient must be established before the corresponding surface emission coefficient can be evaluated. While the same diffusion coefficient can theoretically be obtained from either sorption or desorption curves, the surface emission coefficient for sorption and desorption may not be identical. A well-designed experimental program must be carried out for any quantitative conclusions. The present approach considers the effect of both the condition within the surface of the medium and the external conditions on the surface emission coefficient and is different from the conventional technique that considers the effect of the external or environmental conditions only.

In this paper we derive mathematical equations for surface emission coefficient S in isothermal diffusion analyses of porous solids. The equations are evaluated from either experimental sorption or desorption curves, which are also used to derive the diffusion coefficient D as a function of the concentration of diffusing substance C [1,2,3].

Newman [4] solved the diffusion equation by assuming that both D and S are constants. In many systems, (for example, the diffusion of organic vapors in high-polymer substances [3] and the diffusion of moisture in wood [5]), D depends on C . Crank [3] showed that when S is infinite, values of Newman's constant D evaluated from a set of sorption curves, each corresponding to a different vapor pressure, can be used to derive $D(C)$. The value of the constant D for each curve is evaluated at the time when the fraction of total concentration in the medium E reaches 0.5, a procedure called the half-time technique [3]. Liu [1] presented an analytical method to separate D from S in Newman's solution for desorption. Liu [2] also used the same method to separate D from S for sorption to obtain $D(C)$ using the half-time technique. Liu's results [1,2] agree with the diffusion theory that assumes that $D(C)$ is the same in sorption and desorption. Thus, the accuracy of the half-time technique [3] is analytically established.

Expressing $D(C)$ as an exponential function [6], we now extend Liu's analyses [1,2] to derive mathematical equations for S in sorption and desorption. Mathematical expressions for S corresponding to other functions of $D(C)$ as presented by Crank [3] can likewise be derived. Results should be useful in verifying or improving the conventional expression for S as a function of Reynolds number, Schmidt number, and others, which are related to properties of the external environment only [7], or the recent expression for S that assumes both D and S as constants in problems of diffusion in porous solids [8].

BASIC EQUATIONS AND ANALYSES

In a one-dimensional formulation with the diffusing substance moving in the direction normal to a sheet of a porous medium of thickness $2a$, the diffusion equation can be written as

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial X} \left(D_1 \frac{\partial C}{\partial X} \right) \quad (0 < X < a, \quad t > 0) \quad (1)$$

where C is concentration of the diffusing substance, t is time, D_1 is diffusion coefficient assumed to be an exponential function of C in this study, and X is space coordinate measured from the center of the sheet.

Let the initial condition be

$$C = C_0 \quad (0 < X < a, \quad t = 0) \quad (2)$$

where C_0 is a constant concentration in the medium, and let the boundary conditions be

$$\frac{\partial C}{\partial X} = 0 \quad (X = 0, \quad t \geq 0) \quad (3)$$

$$D_1 \frac{\partial C}{\partial X} = S(C_e - C) \quad (X = a, \quad t > 0) \quad (4)$$

where S is surface emission coefficient and C_e is equilibrium concentration corresponding to the vapor pressure in the atmosphere remote from the surface. Note that Equation (4) prescribes the boundary condition just within the surface of the sheet but not at the surface [3].

Although Equations (1) to (4) apply to sorption when, in Equation (4), $C_e > C$ and to desorption when $C_e < C$, the two cases are different in dimensionless formulation.

Sorption

Let $c = (C - C_0) / (C_e - C_0)$, $D_1 = D_0 \exp(kc)$, where D_0 and k are constants, $D = D_1 / D_0$, $t = D_0 t / a^2$, and $x = X/a$. Equations (1) to (4) can be put in dimensionless form in the same order as follows:

$$\frac{\partial c}{\partial \tau} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \quad (0 < x < 1, \tau > 0) \quad (5)$$

$$c = 0 \quad (0 < x < 1, \tau = 0) \quad (6)$$

$$\frac{\partial c}{\partial x} = 0 \quad (x = 0, \tau \geq 0) \quad (7)$$

$$\frac{D}{L} \frac{\partial c}{\partial x} + c = 1 \quad (x = 1 - \varepsilon, \tau > 0) \quad (8)$$

where L is transport ratio defined as $L = aS/D_0$ and $\varepsilon \gg 0$.

Desorption

Let $c = (C - C_e) / (C_0 - C_e)$, and D_1 , D , t , and x be defined the same as in the case for sorption. Equations (1) to (4) can likewise be put in dimensionless form in the same order as follows:

$$\frac{\partial c}{\partial \tau} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \quad (0 < x < 1, \tau > 0) \quad (9)$$

$$c = 1 \quad (0 < x < 1, \tau = 0) \quad (10)$$

$$\frac{\partial c}{\partial x} = 0 \quad (X = 0, t \geq 0) \quad (11)$$

$$\frac{D}{L} \frac{\partial c}{\partial x} + c = 0 \quad (x = 1 - \varepsilon, \tau > 0) \quad (12)$$

MATHEMATICAL DEVELOPMENT

Mathematical procedures for sorption and desorption are essentially the same. We shall consider the desorption case in detail and list only the results for the sorption case at the end of the section.

Let total concentration in the medium, M , be

$$M(\tau) = \int_0^{1-\varepsilon} c(\tau, x) dx \quad (\varepsilon \rightarrow 0) \quad (13)$$

The fraction of total concentration in the medium is then

$$E = \frac{M(\tau)}{M(0)} \quad (14)$$

From Equations (9) and (11) to (14), we obtain

$$\begin{aligned} \frac{dE}{d\tau} &= \frac{1}{M(0)} \frac{d}{d\tau} \int_0^{1-\varepsilon} c(\tau, x) dx = \frac{1}{M(0)} \int_0^{1-\varepsilon} \frac{\partial c(\tau, x)}{\partial \tau} dx = \frac{1}{M(0)} \int_0^{1-\varepsilon} \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) dx \\ &= \frac{D}{M(0)} \frac{\partial c(\tau, x)}{\partial x} \Big|_0^{1-\varepsilon} = -\frac{L}{M(0)} c(\tau, 1-\varepsilon) \end{aligned} \quad (15)$$

Then, we obtain from Equations (14) and (15)

$$E + \frac{1}{L} \frac{dE}{d\tau} = E \left[\frac{d(\tau + (1/L) \ln E)}{d\tau} \right] = \frac{1}{M(0)} [M(\tau) - c(\tau, 1-\varepsilon)] \quad (16)$$

We can write Equation (16) as

$$E \left[\frac{d(\tau + (1/L) \ln E)}{d\tau} \right] - \frac{1}{M(0)} [M(\tau) - c(\tau, 1-\varepsilon)] = 0 \quad (17)$$

and make use of Equations (13) and (14) to obtain

$$\frac{1}{M(0)} \int_0^{1-\varepsilon} \left\{ c(\tau, x) \frac{d(\tau + (1/L) \ln E)}{d\tau} - [c(\tau, x) - c(\tau, 1-\varepsilon)] \right\} dx = 0 \quad (18)$$

Taking the derivative of Equation (18) with respect to $(\tau + (1/L) \ln E)$ yields

$$\begin{aligned} \int_0^{1-\varepsilon} \left\{ \frac{\partial c(\tau, x)}{\partial (\tau + (1/L) \ln E)} \frac{d(\tau + (1/L) \ln E)}{d\tau} + c(\tau, x) \frac{\partial}{\partial (\tau + (1/L) \ln E)} \right. \\ \left. \times \frac{d(\tau + (1/L) \ln E)}{d\tau} - \frac{\partial [c(\tau, x) - c(\tau, 1-\varepsilon)]}{\partial (\tau + (1/L) \ln E)} \right\} dx = 0 \end{aligned} \quad (19)$$

From Equations (14) and (15), the derivative of $(1/L) \ln E$ with respect to τ is negligible compared with 1. This is also true when the diffusion coefficient is a constant [1,2]. Therefore, the second term in Equation (19) can be neglected, and we obtain

$$\int_0^{1-\varepsilon} \left\{ \frac{\partial c(\tau, x)}{\partial \tau} - \frac{\partial [c(\tau, x) - c(\tau, 1-\varepsilon)]}{\partial (\tau + (1/L) \ln E)} \right\} dx = 0 \quad (20)$$

Substituting Equation (9) into Equation (20) yields

$$\begin{aligned} \int_0^{1-\varepsilon} \left\{ \frac{\partial}{\partial x} \left(D \frac{\partial c(\tau, x)}{\partial x} \right) - \frac{\partial [c(\tau, x) - c(\tau, 1-\varepsilon)]}{\partial (\tau + (1/L) \ln E)} \right\} dx = 0 \\ \int_0^{1-\varepsilon} \left\{ \frac{\partial}{\partial x} \left(D \frac{\partial [c(\tau, x) - c(\tau, 1-\varepsilon)]}{\partial x} \right) - \frac{\partial [c(\tau, x) - c(\tau, 1-\varepsilon)]}{\partial (\tau + (1/L) \ln E)} \right\} dx = 0 \end{aligned} \quad (21)$$

If we set

$$c'(\tau', x) \equiv c(\tau, x) - c(\tau, 1 - \varepsilon) \quad (22)$$

and

$$\tau' \equiv \tau + \frac{1}{L} \ln E \quad (23)$$

we obtain from Equation (21)

$$\int_0^{1-\varepsilon} \left[\frac{\partial}{\partial x} \left(D \frac{\partial c'}{\partial x} \right) - \frac{\partial c'(\tau', x)}{\partial \tau'} \right] dx = 0 \quad (24)$$

which is satisfied if

$$\frac{\partial c'}{\partial \tau'} = \frac{\partial}{\partial x} \left(D \frac{\partial c'}{\partial x} \right) \quad (0 < x < 1, \tau' > 0) \quad (25)$$

Equation (25) has the same form as Equation (9). We must find the initial and boundary conditions for Equation (25) from Equations (10) to (12) by means of Equations (22) and (23).

From Equations (10), (22), and (23), we find

$$c' = 0 \quad (0 < x < 1, \tau' = 0) \quad (26)$$

From Equations (11) and (22), we find

$$\frac{\partial c'}{\partial x} = 0 \quad (x = 0, \tau' \geq 0) \quad (27)$$

From Equations (12) and (22), we obtain

$$\frac{D}{L} \frac{\partial c'}{\partial x} + c' = \frac{D}{L} \frac{\partial c'}{\partial x} + c(\tau, 1 - \varepsilon) - c(\tau, 1 - \varepsilon) = 0$$

or

$$\frac{D}{L} \frac{\partial c'}{\partial x} = 0 \quad (x = 1 - \varepsilon', \tau' > 0) \quad (28)$$

Since $D \partial c' / \partial x \neq 0$, we must have $L \rightarrow \infty$ to satisfy Equation (28). However, this result does not give the needed boundary condition. Comparing Equations (25) to (27) with Equations (5) to (7), we see a one-to-one correspondence. The needed boundary condition must then be obtained from Equation (8). If we set $L \rightarrow \infty$ in Equation (8), we have $c = 1$ at $x = 1 - \varepsilon$ and $\tau > 0$. Thus, we obtain the boundary condition replacing Equation (28) as

$$c' = 1 \quad (x = 1 - \varepsilon', \tau' > 0) \quad (29)$$

The justification of Equation (29) as the needed boundary condition exists in the fact that the boundary condition is defined just within the surface but not at the surface [3]. Therefore, if we consider Equation (8) to be true at $x = 1 - \varepsilon$ with $\varepsilon \rightarrow 0$, we can consider Equation (29) to be true at $x = 1 - \varepsilon'$ with $\varepsilon' < \varepsilon$, and all the boundary conditions are satisfied.

If, with k in D being a constant, $\tau = \tau(L, E)$ and $\tau' = t'(L, E')$, then we obtain from Equation (23)

$$\tau'(\infty, E') = \tau(L, E) + \frac{1}{L} \ln E \quad (30)$$

where τ' and E' are associated with sorption and τ , E , and L with desorption.

Let L' be associated with sorption. Following the same analytical procedures, the corresponding equation for sorption becomes

$$\tau(\infty, E) = \tau'(L', E') + \frac{1}{L'} \ln E' \quad (31)$$

The surface emission coefficients, S for desorption and S' for sorption, which are contained in L and L' , respectively, can now be expressed from Equations (30) and (31) as follows:

for desorption,

$$S = \frac{D_0}{a} \left[\frac{\ln E}{\tau'(\infty, E') - \tau(L, E)} \right] \quad (32)$$

for sorption,

$$S' = \frac{D_0}{a} \left[\frac{\ln E'}{\tau(\infty, E) - \tau'(L', E')} \right] \quad (33)$$

We note in the above equations

$$E + E' = 1 \quad (34)$$

$$\tau(L, E) = \frac{D_0 t}{a^2} \quad (35)$$

$$\tau'(L', E') = \frac{D_0 t'}{a^2} \quad (36)$$

In Equations (35) and (36), t and t' are to be evaluated from experimental desorption- and sorption-time curves corresponding to specified values of E and E' , respectively. The $\tau'(\infty, E')$ in Equation (32) and $\tau(00, E)$ in Equation (33) are to be evaluated using numerical techniques.

NUMERICAL RESULTS AND DISCUSSION

Using a finite difference approach, $\tau'(\infty, E')$ for sorption were calculated from Equations (5) to (8) with $L \rightarrow \infty$ for different values of k . We note here the relevant parameters in Equations (5) to (8) are denoted by primes to differentiate them from those for desorption. Results are plotted in Figure 1. Results of $\tau(\infty, E)$ for desorption have been likewise obtained from Equations (9) to (12) and are plotted in Figure 2.

Although Equations (32) and (33) are true for any values of E and E' under the condition of Equation (34), we need to set $E = E' = 0.5$ in accordance with the half-time technique. This technique has yielded the result [1,2] that the same diffusion coefficient can be obtained from either sorption or desorption curves. Also, a preliminary analysis of some sorption data for aspen [9] tends to support the assumption that S' is a constant: for the same set of sorption curves, each corresponding to a different vapor pressure, the S' values for the curves are approximately the same when evaluated at $E' = 0.5$.

From Figure 3, $\tau'(\infty, 0.5)$ is seen to be smaller than $\tau(\infty, 0.5)$ for any specified value of k . Therefore, S in Equation (32) and S' in Equation (33) are not necessarily the same. According to

experimental data from red oak [6], t in Equation (35) for $E = 0.5$ and t' in Equation (36) for $E' = 0.5$ are approximately equal. Assuming that $\tau(L, 0.5) = \tau(L', 0.5)$, Equations (32) and (33) would yield $S' > S$. However, more specially designed series of experiments need be conducted to obtain quantitative results.

CONCLUSIONS

The surface emission coefficient and the diffusion coefficient as a function of the concentration of diffusing substance may be derived from experimental sorption or desorption curves using the half-time technique. Although they may be obtained from the same experimental diffusion data, the diffusion coefficient must be derived first to provide the additional information needed for deriving the surface emission coefficient.

The same diffusion coefficient is derived from either sorption or desorption curves for the same medium, but the surface emission coefficients for sorption and desorption may take different values.

In the literature, it is generally assumed that the surface emission coefficient is a function of external or environmental conditions only, not of the material properties of the medium. The present study shows that the surface emission coefficient is a function of both the environmental conditions and the medium properties.

NOTATION

a	Half-thickness of medium
C	Concentration of diffusing substance
C_e	Equilibrium concentration of diffusing substance
C_0	Initial concentration of diffusing substance
c, c'	Dimensionless concentration of diffusing substance
D	Dimensionless diffusion coefficient
D_1	Diffusion coefficient as an exponential function of c
E, E'	Fraction of total concentration in medium
L, L'	Transport ratio
M	Total concentration in medium
S, S'	Surface emission coefficient
t	Time
X	Space coordinate
x	Dimensionless space coordinate
ϵ, ϵ'	Positive constant close to zero
τ, τ'	Dimensionless time

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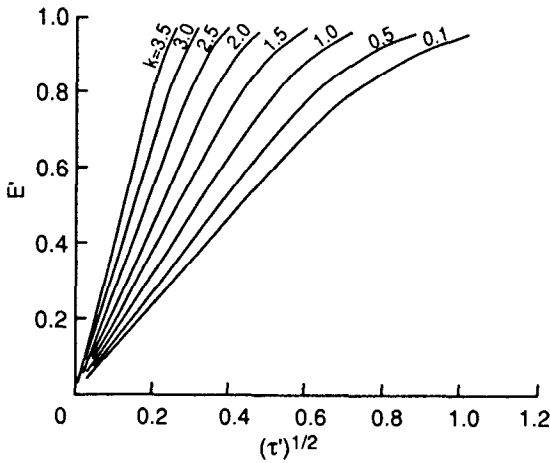


Figure 1—Sorption curves for exponential diffusion coefficient $D_1 = D_0 \exp(kc)$ and dimensionless time $\tau' = \tau'(\infty, E')$.

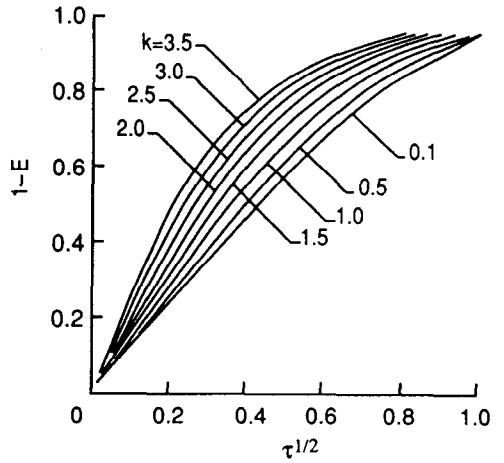


Figure 2—Desorption curves for exponential diffusion coefficient $D_1 = D_0 \exp(kc)$ and dimensionless time $\tau = \tau(\infty, E)$.

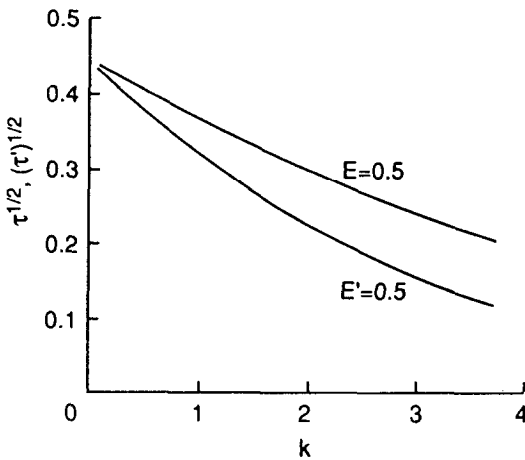


Figure 3— $[\tau(\infty, E)]^{1/2}$ for desorption and $[\tau'(\infty, E')]^{1/2}$ for sorption as functions of k in diffusion coefficient $D_1 = D_0 \exp(kc)$.