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Diffusion Coefficient of Porous Solid Obtained From Isothermal Sorption Tests

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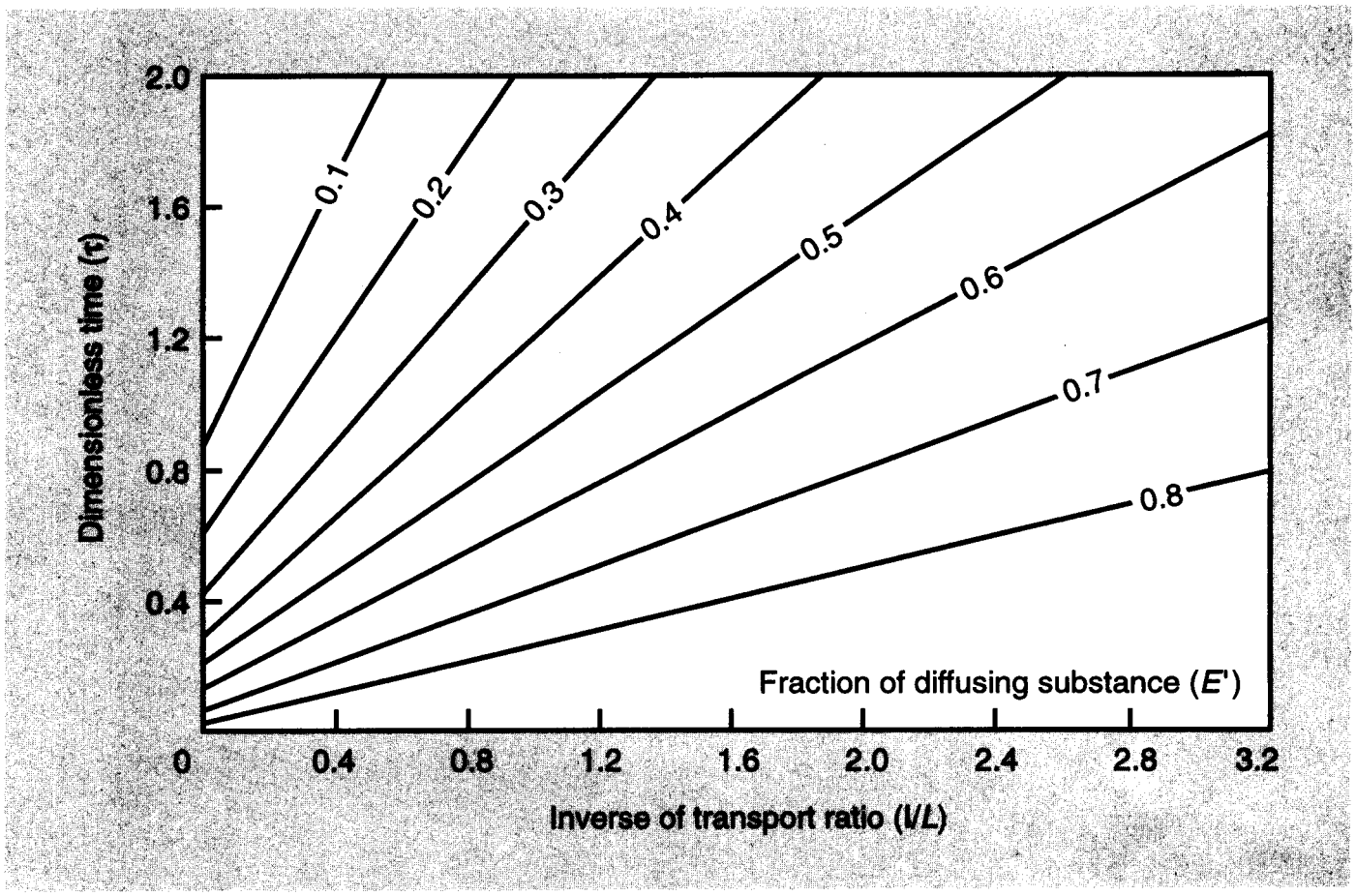

Abstract

In this study, a mathematical equation was derived to separate the diffusion coefficient and the surface emission coefficient in Newman's solution of the unsteady-state diffusion equation from an experimental sorption curve. Based on this derived equation, a theoretical expression for the diffusion coefficient was also derived. Results of the present study for sorption complement those of a previous study for desorption. Corresponding resulting equations for sorption and desorption are not the same, and application of these equations must be carried out with discretion.

Keywords: Concentration of diffusing substance, diffusion coefficient, diffusion equation, surface emission coefficient

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Diffusion Coefficient of Porous Solid Obtained From Isothermal Sorption Tests

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Introduction

This paper presents a mathematical equation that can be used to separate the diffusion coefficient *D* and surface emission coefficient *S* in Newman's solution of the unsteady-state diffusion equation (Newman 1931). The separation is achieved using an experimental sorption curve that presents the average amount of diffusing substance in a medium versus time in a sorption process. This study is a necessary complement to a previous study by Liu (1993) in which a corresponding mathematical equation was derived for the case of desorption, because the sorption process has special advantages (Felder and Huvard 1980) and the derived equations for desorption and sorption are not the same.

For certain porous solids such as wood, the thermal diffusion coefficient can be orders of magnitude higher than the moisture diffusion coefficient (Liu 1991). In the process of drying, we can assume that the temperature in such a medium is uniform and apply the isothermal diffusion theory to predict the time-dependent distribution of the diffusing substance *C* in the medium. Therefore, it is very important to study the properties of the diffusion coefficient *D* to apply the diffusion theory with the desired results.

The diffusion coefficients of many solids including wood show a strong concentration dependence (Hougen and others 1940, Van Arsdel 1947, Skaar 1954, Meroney 1969). The influence of temperature on *D* is typically expressed as an activation energy based on the Arrhenius equation (Waananen and others 1993). In Newman's solution, both *D* and *S* are assumed to be constant. From a set of sorption or desorption curves, each curve corresponding to a different pressure of the surrounding medium in the testing environment, we obtain a set of constant values for *D* and *S;* each pair of *D* and *S* values corresponds to a different curve, Following the half-time technique by Crank (1975), the constant *D* values thus obtained can be used to derive *D* as a function of *C*.

Crank and Park (1949) presented a set of curves obtained experimentally for the uptake of chloroform by a polystyrene sheet; each curve corresponded to a different vapor pressure. Crank (1975) used Newman's solution with the assumption that *S* was infinity to obtain the constant *D* for each curve and then derived *D* as a function of the concentration of chloroform. However, in many practical sorption or desorption tests, the value for *S* is finite. In those cases, the analytical procedure in Crank (1975) cannot be applied directly to derive a concentration-dependent diffusion coefficient *D(C)*.

The mathematical equation derived in the present study provides the missing link in applying Crank's half-time technique (Crank 1975) to derive *D(C)* for a finite *S* and includes the assumption of an infinite *S* as a special case in the sorption process. Because the diffusion coefficient of a porous solid can be obtained from either sorption or desorption tests, the resulting formula for *D* in the present study for sorption also verifies the corresponding formula in Liu (1993) for desorption.

Basic Equations and Analyses

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

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

where C is concentration of the diffusing substance, t is time, D *is* diffusion coefficient assumed to be a constant in this study, and X is space coordinate measured from the center of the sheet.

Let the initial condition be

$$C = C_0 \qquad (0 < X < a,\ t = 0) \tag{2}$$

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

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

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

where S is surface emission coefficient and C_e is equilibrium concentration corresponding to the vapor pressure in the atmosphere remote from the surface. Equation (4) prescribes the boundary condition just within the surface of the sheet but not at the surface (Crank 1975).

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 $c = (C - C_0)/(C_e - C_0)$, $\tau = Dt/a^2$, and $x = X/a$. Equations (1) to (4) can be put in dimensionless form in the same order as previously presented:

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial x^2} \qquad (0 < x < 1,\ \tau > 0) \tag{5}$$

$$c = 0 \qquad (0 < x < 1,\ \tau = 0) \tag{6}$$

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

$$\frac{1}{L}\frac{\partial c}{\partial x} + c = 1 \qquad (x = 1 - \epsilon,\ \tau > 0) \tag{8}$$

where L is transport ratio defined as $L = aS/D$ and $\epsilon \to 0$.

Desorption

Let $c = (C - C_e)/(C_0 - C_e)$, $\tau = (Dt/a^2)$, and $x = (X/a)$. Equations (1) to (4) can likewise be put in dimensionless form in the same order as previously presented:

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial x^2} \qquad (0 < x < 1,\ \tau > 0) \tag{9}$$

$$c = 1 \qquad (0 < x < 1,\ \tau = 0) \tag{10}$$

$$\frac{\partial c}{\partial x} = 0 \qquad (x = 0, \tau \geq 0) \tag{11}$$

$$\frac{1}{L}\frac{\partial c}{\partial x} + c = 0 \qquad (x = 1 - \epsilon,\ \tau > 0) \tag{12}$$

Mathematical Development

Consider the sorption case. Let

$$M(\tau) = \int_0^{1-\epsilon} c(\tau, x)dx \qquad (\epsilon \to 0) \tag{13}$$

The fraction of total concentration in the medium, E, is then

$$E = \frac{M(\tau)}{M(\infty)} = M(\tau) \qquad (M(\infty) = 1) \tag{14}$$

From Equations (5) to (8), (13), and (14), we obtain

$$\begin{aligned}
\frac{dE}{d\tau} &= \frac{d}{d\tau}\int_0^{1-\epsilon} c(\tau, x)dx \\
&= \int_0^{1-\epsilon} \frac{\partial c(\tau, x)}{\partial \tau}dx \\
&= \int_0^{1-\epsilon} \frac{\partial^2 c(\tau, x)}{\partial x^2}dx \\
&= \left.\frac{\partial c(\tau, x)}{\partial x}\right|_0^{1-\epsilon} \\
&= L[1 - c(\tau, 1-\epsilon)]
\end{aligned} \tag{15}$$

or

$$\frac{1}{L}\frac{d(1-E)}{d\tau} = c(\tau, 1-\epsilon) - 1 \tag{16}$$

Adding (1– E) to both sides of Equation (16) yields

$$\begin{aligned}
(1-E) + \frac{1}{L}\frac{d(1-E)}{d\tau} &= 1 - E + c(\tau, 1-\epsilon) - 1 \\
&= c(\tau, 1-\epsilon) - E
\end{aligned} \tag{17}$$

We can write Equation (17) as

$$(1-E)\left\{\frac{d[\tau + (1/L)\ln(1-E)]}{d\tau}\right\} - \left[c(\tau, 1-\epsilon) - E\right] = 0 \tag{18}$$

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

$$\int_0^{1-\epsilon}\left\{\left[1 - c(\tau, x)\right]\frac{d[\tau + (1/L)\ln(1-E)]}{d\tau} - \left[c(\tau, 1-\epsilon) - c(\tau, x)\right]\right\}dx = 0 \tag{19}$$

Taking the derivative of Equation (19) with respect to$[\tau + 1/L\ln(1-E)]$ yields

$$\begin{aligned}
\int_0^{1-\epsilon}\Bigg\{ & \frac{\partial[1 - c(\tau, x)]}{\partial[\tau + (1/L)\ln(1-E)]} \times \frac{d[\tau + (1/L)\ln(1-E)]}{d\tau} \\
& + [1 - c(\tau, x)]\frac{\partial}{\partial[\tau + (1/L)\ln(1-E)]} \times \frac{d[\tau + (1/L)\ln(1-E)]}{d\tau} \\
& - \frac{\partial[c(\tau, 1-\epsilon) - c(\tau, x)]}{\partial[\tau + (1/L)\ln(1-E)]}\Bigg\}dx = 0
\end{aligned} \tag{20}$$

From Equations (14) and (15), the derivative of (l/L) ln(l – *E)* with respect to τ is seen to be negligible compared with unity. We can therefore neglect the second term in Equation (20) and obtain

$$\int_0^{1-\epsilon}\left\{\frac{\partial[1-c(\tau,x)]}{\partial\tau}-\frac{\partial[c(\tau,1-\epsilon)-c(\tau,x)]}{\partial[\tau+(1/L)\ln(1-E)]}\right\}dx=0 \tag{21}$$

Substituting Equation (9) into Equation (21) yields

$$\int_0^{1-\epsilon}\left\{\frac{\partial^2[1-c(\tau,x)]}{\partial x^2}-\frac{\partial[c(\tau,1-\epsilon)-c(\tau,x)]}{\partial[\tau+(1/L)\ln(1-E)]}\right\}dx=0$$

or

$$\int_0^{1-\epsilon}\left\{\frac{\partial^2[1+c(\tau,1-\epsilon)-c(\tau,x)]}{\partial x^2}-\frac{\partial[1+c(\tau,1-\epsilon)-c(\tau,x)]}{\partial[\tau+(1/L)\ln(1-E)]}\right\}dx=0 \tag{22}$$

If we set

$$c'(\tau',x)\equiv 1+c(\tau,1-\epsilon)-c(\tau,x) \tag{23}$$

and

$$\tau'\equiv\tau+\frac{1}{L}\ln(1-E) \tag{24}$$

we obtain from Equation (22)

$$\int_0^{1-\epsilon}\left[\frac{\partial^2 c'(\tau',x)}{\partial x^2}-\frac{\partial c'(\tau',x)}{\partial\tau'}\right]dx=0 \tag{25}$$

which is satisfied if

$$\frac{\partial c'}{\partial\tau'}=\frac{\partial^2 c'}{\partial x^2}\qquad(0<x<1,\ \ \tau'>0)$$

Equation (26) has the same form as Equation (5). We need to find the initial and boundary conditions for Equation (26) from Equations (6) to (8) by means of Equations (23) and (24).

From Equations (6), (23), and (24), we find

$$c'=1\qquad(0<x<1,\ \ \tau>0) \tag{27}$$

From Equations (7), (23), and (24), we obtain

$$\frac{\partial c'}{\partial x}=0\qquad(x=0,\ \ \tau'\geq 0) \tag{28}$$

From Equations (8), (23), and (24), we obtain

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

or

$$\frac{1}{L'}\frac{\partial c'}{\partial x} = 0 \qquad (x = 1 - \epsilon', \ \ \tau' > 0) \tag{29}$$

Because $\partial c'/\partial x \neq 0$, we must have $L' = \infty$ to satisfy Equation (29). However, this result does not provide the needed boundary condition. Comparing Equations (26) to (28) with Equations (9) to (11), we see *a* one-to-one correspondence. The needed boundary condition must then be obtained from Equation (12). If we set $L = \infty$ in Equation (12), we have $c = 0$ at $x = 1 - \epsilon$ and $\tau > 0$. Thus, we obtain the following boundary condition replacing Equation (29):

$$c' = 0 \qquad (x = 1 - \epsilon', \ \ \tau' > 0) \tag{30}$$

The justification of Equation (30) as the needed boundary condition exists in the fact that the boundary condition is defined just within the surface but not at the surface (Crank 1975). Therefore, if we consider Equation (12) to be true at $x = 1 - \epsilon$ with $\epsilon \rightarrow 0$, we can consider Equation (30) to be true at $x' = 1 - \epsilon'$ with $\epsilon' < \epsilon$. Further verification of the accuracy of Equation (30) as the needed boundary condition will be shown in the next section.

If we write

$$\tau = \tau(L, E) \quad \text{and} \quad \tau' = \tau'(L', E')$$

we would obtain from Equation (24)

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

where τ' is associated with desorption and τ with sorption. Therefore, the dimensionless time for sorption defined by Equations (5) to (8) is related to the dimensionless time for desorption defined by Equations (26) to (28) and (30) as

$$\tau(L, E) = \tau'(\infty, E') - \frac{1}{L}\ln(1 - E) \tag{32}$$

We note in Equation (32)

$$E + E' = 1 \tag{33}$$

and solutions corresponding to τ (L, E) and $\tau'(\infty, E')$ are available in Crank (1975). Knowing either E *or* E', the other can be evaluated from Equation (33).

Numerical Verification and Application

The solution to Equation (5) under the conditions of Equations (6) to (8) can be found in Crank (1975) as

$$E = 1 - 2L^2 \sum_{n=1}^{\infty} \frac{\exp(-\beta_n^2 \tau)}{\beta_n^2(\beta_n^2 + L^2 + L)} \tag{34}$$

in which β_n are the positive roots of

$$\beta_n \tan \beta_n = L \tag{35}$$

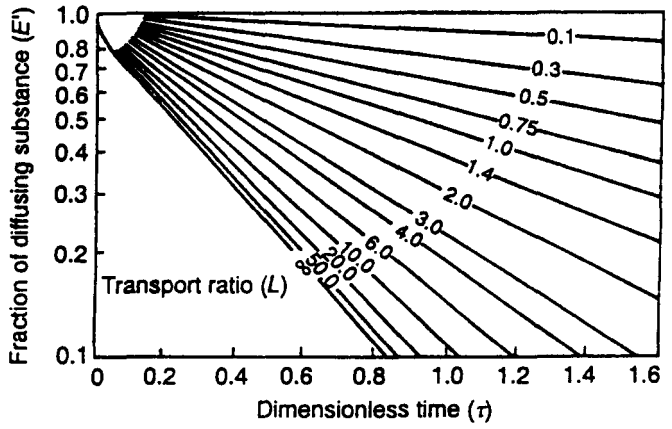

Figure 1—Fraction of diffusing substance in medium in desorption, as a function of dimensionless time for various values of transport ratio (Skaar 1954).

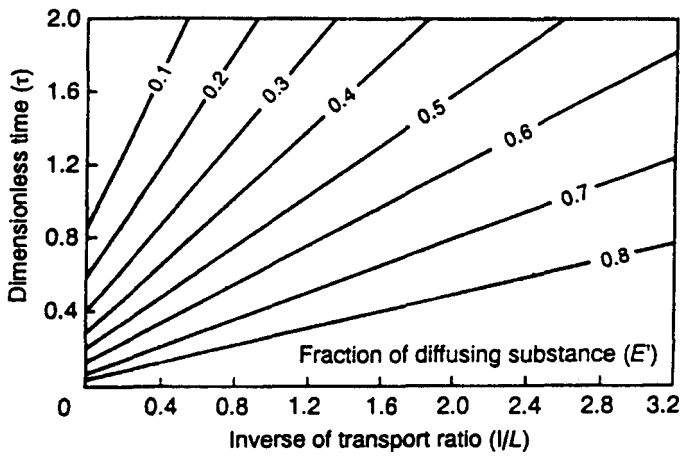

Figure 2—Dimensionless time as a function of inverse of transport ratio for various values of fraction of diffusing substance in medium in desorption.

For various values of L, the relationship between $(1 - E)$ or E' for desorption and τ in Equation (34) was obtained by Newman (1931) and plotted by Skaar (1954) (Fig. 1) for determining the coefficient of moisture diffusion in wood.

From studying the separation of diffusion and surface emission coefficients in moisture desorption of wood, Liu (1989) obtained from Equation (34) the relationship between τ and $1/L$ for various values of E' (Fig. 2). The straight lines in Figure 2 also verify the linear relationship between τ and $1/L$ for various values of E in Equation (32) for sorption, because the line for $E' = k$ is also the line for $E = (1 - k)$ in Figure 2.

To evaluate $\tau'(\infty, E')$ in Equation (32), we need to solve Equation (26) under the conditions of Equations (27), (28), and (30). The solution can be found in Crank (1975) as

$$E' = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp[-(n + \frac{1}{2})^2 \pi^2 \tau'] \tag{36}$$

For small times or $E' \geq 0.5$, Equation (36) can be approximated by

$$\tau'(\infty, E') = \frac{\pi(1 - E')^2}{4} \tag{37}$$

For large times or $E' < 0.5$, Equation (36) can be approximated by

$$\tau'(\infty, E') = -\frac{4}{\pi^2} \ln\left(\frac{\pi^2 E'}{8}\right) \tag{38}$$

When Equation (37) or (38) is substituted into Equation (32) with E' replaced by $(1 - E)$ according to Equation (33), the results agree with those shown in Figure 2. Of course, we must also replace E' in Figure 2 by $(1 - E')$ to demonstrate the agreement. Thus, we have also obtained numerical verification of the accuracy of Equation (30).

Equation (32) can be used to separate D and S using a sorption curve. The D values obtained from a set of sorption curves, each curve corresponding to a different vapor pressure, and evaluated at half-times (that is, times corresponding to $E = 0.5$), can be used to derive the concentration-dependent diffusion coefficient $D(C)$ as described by Crank (1975). To show how D can be separated from S, let us first write Equation (32) in the following form:

$$\tau = A + \frac{B}{L} \tag{39}$$

where

$$A = \tau'(\infty, E') \tag{40}$$

and

$$B = -\ln(1 - E) \tag{41}$$

We need to use a typical sorption curve with fraction of diffusing substance E as a function of time t as shown in Figure 3. In Figure 3, E_1 and E_2 are two values on the curve corresponding to t_1 and t_2. Writing τ in explicit form, we obtain from Equation (39)

$$\frac{Dt_1}{a^2} = A_1 + \frac{B_1}{L} \tag{42}$$

$$\frac{Dt_2}{a^2} = A_2 + \frac{B_2}{L} \tag{43}$$

where A and B are subscripted in correspondence with E or t, and D, a, and L are constants.

Eliminating L from Equations (42) and (43) yields

$$\frac{D}{a^2} = \frac{A_1/B_1 - A_2/B_2}{t_1/B_1 - t_2/B_2} \tag{44}$$

Because A, B, and t all vary with E, as E_1 and E_2 approach 0.5 from opposite directions in Figure 3, Equation (44) can be put in the form

$$\frac{D}{a^2} = \left.\frac{d(A/B)/dE}{d(t/B)/dE}\right|_{E=0.5} \tag{45}$$

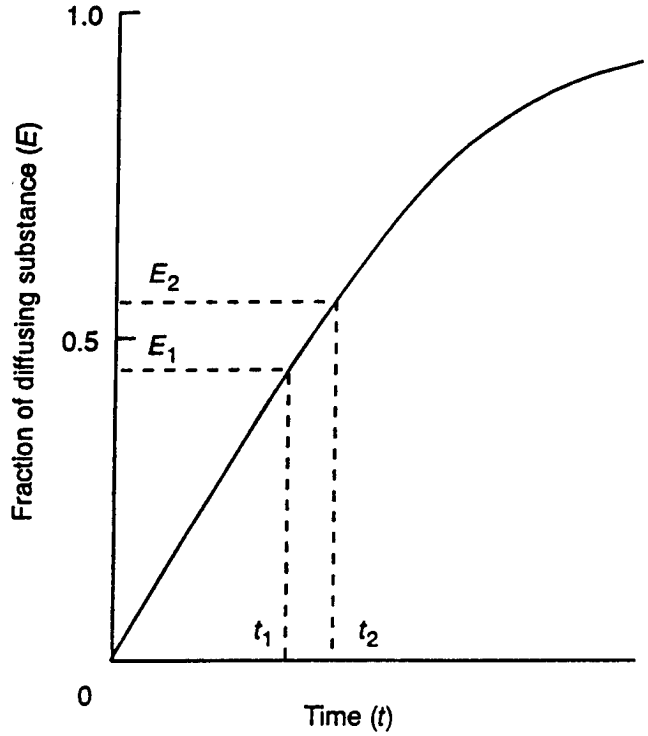

Figure 3—Typical sorption curve showing fraction of diffusing substance in medium as a function of time.

which is evaluated at $E = 0.5$.

Equation (45) can be expanded and simplified to

$$\frac{D}{a^2} = \left.\frac{B(dA/dE) - A(dB/dE)}{B(dt/dE) - t(dB/dE)}\right|_{E=0.5} \tag{46}$$

Using Equations (37), (40) with E' replaced by $(1 - E)$, and (41), we obtain from Equation (46)

$$\frac{D}{a^2} = \left.\frac{0.1517}{0.6931(dt/dE) - 2t}\right|_{E=0.5} \tag{47}$$

When we substitute $t = \pi a^2/16D$ and $dt/dE = \pi a^2/4D$ obtained from Equation (37) into Equation (47), we find Equation (47) is satisfied. Once D is obtained from Equation (47), L can be evaluated from Equation (39) with $E = 0.5$ and S from the definition of L following Equation (8). However, the application of the constant S values obtained is beyond the scope of this study.

The formula for D derived from the desorption analysis in Liu (1993) has the form

$$\frac{D}{a^2} = \left.\frac{-0.1517}{0.6931(dt/dE') + 2t}\right|_{E'=0.5} \tag{48}$$

In Equations (47) and (48), the t's are the same. In Equation (47), dt/dE is positive, and in Equation (48), dt/dE' is negative; but dt/dE and dt/dE' have the same absolute value. This can easily be deduced from Equations (34) and (36) as well as from

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Figure 1. Therefore, the constant D value in Newman's solution can be obtained from either Equation (47) for sorption or Equation (48) for desorption.

Conclusions

The dimensionless time of Newman's solution for sorption as shown in Equation (32) is different from the corresponding equation for desorption in Liu (1993). The formula for D in Equation (47) derived from Equation (32) for sorption is also different from the corresponding formula for D in Equation (48) derived in Liu (1993) for desorption. The input data for Equation (47) are not the same as those for Equation (48). With the correct input data, both Equations (47) and (48) yield the same value for D *as* they should. The differentiation of Equations (47) and (48) must be carefully observed to generate a set of correct D values from an appropriately designed test program. The set of D values can be used to derive $D(C)$ using the half-time technique whatever the relationship between D and C (Crank 1975).

For nonhomogeneous porous solids such as wood, obtaining a representative sorption or desorption curve is necessary to accurately evaluate D and S for each set of specified test conditions.

Nomenclature

A Function of E'

a Half of medium thickness

B Function of E

C Concentration of diffusing substance

C_e Equilibrium concentration of diffusing substance

C_o Initial concentration of diffusing substance

c, c' Dimensionless concentration of diffusing substance

D Diffusion coefficient

E Fraction of total concentration in medium in sorption

E' Fraction of total concentration in medium in desorption

L, L' Transport ratio

M Total concentration in medium

S Surface emission coefficient

t Time

X Space coordinate

x Dimensionless space coordinate

Greek Symbols

ϵ, ϵ' Positive constant close to zero

τ, τ' Dimensionless time

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