

A Simple Equation for Determining the Diffusion Coefficient from the Time of Half Sorption

In describing the kinetics of diffusion-controlled processes, the rate is characterized by the diffusion coefficient.

In the case of diffusion into fibers (which are considered to be an infinite cylinder with radius r) from an efficiently stirred finite bath, the diffusion coefficient is expressed as

$$D = (r^2/t)f(E_s, R_t) \quad (1)$$

where E_s is equilibrium fractional exhaustion, R_t is dimensionless amount of penetrant in the fiber, and f expresses the certain function attachment. Further,

$$R_t = M_t/M_\infty \quad (2)$$

and

$$E_s = (C_0 - C_\infty)/C_0 = M_\infty/VC_0 = (\alpha + 1)^{-1} \quad (3)$$

where M_t is the amount of penetrant in the fibre at time t , M_∞ is the amount of penetrant in the fiber at equilibrium ($t \rightarrow \infty$), C_0 is the initial (equilibrium) concentration of penetrant (C_∞) in surrounding volume V , and α is the parameter related to volume V and to that of the fibers.³

The known solution of Fick's second law for this case was pubhed for $E_s = 0$ and for $0 < E_s < 1$.^{1,2} Both resulting expressions represent sums of exponentials where D is an exponent and cannot be expressed explicitly in the form of eq. (1).

The diffusion coefficient is then calculated either by direct iteration from the series or using tables and graphs.⁴ There are also publications^{5,6,8,9} where Hill or Wilson exponential series are substituted with simpler analytic functions which can usually be transformed into eq. (1).

Further simplification may be obtained by introducing a characteristic value for the sorption process into eq. (1). One of the easily determined values for the sorption processes is the point of half-sorption, which approximately characterizes the whole course of absorption in a particular system.⁸ The time corresponding to the point of half-sorption is called the time of half-sorption $t_{1/2}$.

It denotes the time when the fibers absorb half of the equilibrium amount of penetrant, i.e., $R_t = 0.5$. Substituting $R_t = 0.5$ and $t = t_{1/2}$ into eq. (1), the expression is simplified as follows:

$$D = r^2/t_{112}f_1(E_s) \quad (4)$$

or

$$T_{1/2} = f_1(E_s) \quad (4a)$$

where $T_{1/2} = Dt_{1/2}r^{-2}$ is the dimensionless time of half-sorption (an analogy to the Fourier number). Dependence (4) cannot be obtained explicitly from either the Hill or the Wilson series, and therefore it is necessary to use certain approximations.

An expression (valid only in the narrow range of E_s) approximating the dependence (4) was proposed by Kilby.⁸

Silova and Melnikov⁷ introduced two equations, one for the range $0 \leq E_s \leq 0.9$; the other for $0.9 < E_s < 1$. Neither of these expressions covers the whole range E_s with suitable accuracy. On the basis of our approximate diffusion equation (9), we proposed the expression

$$T_{1/2} = [K_1/(1 - E_s) + K_2]^{-2} \quad (5)$$

Equation (5) was used for nonlinear approximation of the dependence $T_{1/2}$ on fractional equilibrium exhaustion E_s in the range $0 \leq E_s \leq 0.9$. The true values of $T_{1/2}$ were calculated iteratively^{12,13} from the Wilson ($0 < E_s < 0.9$) or Hill ($E_s = 0$) series.² The constants K_1 and K_2 were determined so that eq. (5) is the best approximation of $T_{1/2}$ on E_s dependence in the sense of mean relative deviation.

The modified optimization procedure without derivatives based on the pattern search method¹¹ was applied for minimization. The resulting expression

$$T_{1/2} = [2.64/(1 - E_s) + 1.36]^{-2} \quad (6)$$

approximates the dependence of true $T_{1/2}$ on E_s with an average relative deviation of 0.53%. Relation (6) was checked with the dependence $T_{1/2}$ on E_s presented by Kilby.⁸ It was verified that eq. (6) is convenient in the range of $0 \leq E_s \leq 0.999$ (maximal relative deviation of approximation is less than 3%).

In summary, a very simple eq. (6) may be used to determine the apparent diffusion coefficient from the time of half-sorption within the whole range of the equilibrium fraction exhaustion.

References

1. A. V. Hill, *Proc. R. Soc.*, **B104**, 39 (1928).
2. A. H. Wilson, *Philos. Mag.*, **39** 48 (1948).
3. J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1956, pp. 70–71.
4. T. Vickerstaff, *The Physical Chemistry of Dyeing*, 2nd ed., Oliver Boyd, London, 1954, Chap. 5.
5. H. Ynoue and Y. Suda, *Sen-i Gakkaishi*, **24**, 88 (1968).
6. H. Udeaira, *Sen-i Gakkaishi*, **14**, 481 (1958).
7. G. I. Silova and B. N. Melnikov, *Izv. Vysc. Uc. Zav. Technol. Text. Prom.*, No. 5, 87 (1972).
8. W. F. Kilby, *J.S.D.C.*, **76** 479 (1960).
9. J. Rais and J. Militký, *J.S.D.C.*, **91**, 344 (1975).
10. J. Boulton and (Miss) Reading, *J.S.D.C.*, **50**, 381 (1934).
11. J. Militký, Programme "Wilde", *Unified Software System*, VÚZ Dvůr Králové, July 1976.
12. J. Militký, Programme "Wilson", *Unified Software System*, VÚZ Dvůr Králové, September 1976.
13. J. Militký, Programme "Hill", *Unified Software System*, VÚZ Dvůr Králové, October 1976.

JIŘÍ MILITKÝ

Research Institute for Textile Finishing
544 00 Dvůr
Králové n. Labem, Czechoslovakia

JIRÍ RAIS

College of Textile Engineering
Liberec, Czechoslovakia

Received April 17, 1978
Revised July 24, 1978