A Rate Equation for Molecular Diffusion in a Dispersed Phase

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Clarification appears necessary for the rate equation for molecular diffusion within a dispersed phase such as that of a granular solid or a relatively stagnant drop of fluid. One encounters, in connection with theoretical developments concerning this type of diffusion, statements that it has been "assumed" that a rate equation of the form

$$\text{rate} = \text{constant}\ (W^* - W) \qquad (1)$$

is applicable. Here

W = average concentration of a solute in a dispersed phase
W^* = average concentration on the dispersed-phase side of the interface between dispersed and continuous phase

An effort is made in this note to elucidate the conditions under which Equation (1) is applicable. The constant in Equation (1) is normally represented by the symbol ka with the units of reciprocal time. Specification of the true physical composition of ka follows as a by-product of the foregoing effort. Further a substitute rate equation is given for the shorter time intervals wherein rate equation (1) fails.

Wicke (*1*) in his treatment of a similar problem regarding an adsorbent granule came close to clarifying the situation without actually having recognized a basic conclusion of his work.

The governing equation for diffusion in a sphere of dispersed phase is

$$\frac{\partial C_s}{\partial t} = D\left[\frac{\partial^2 C_s}{\partial r^2} + \frac{2}{r}\frac{\partial C_s}{\partial r}\right] \qquad (2)$$

where

C_s = point concentration of a solute in the sphere, mole/cu. ft.
D = molecular diffusivity of mass, sq. ft./hr.
r = radial position in sphere, ft.
t = time, hr.

The limiting conditions are

$$\begin{aligned} C_s(r, o) &= C_i, \text{ a constant} \\ C_s(o, t) &= \text{a maximum or minimum} \qquad (3) \\ C_s(R, t) &= C_s^*(t) \end{aligned}$$

where

R = radius of the sphere, ft.

If for convenience one defines

$$U(r, t) = rC_s(r, t) \qquad (4)$$

then

$$\frac{\partial U}{\partial t} = D\frac{\partial^2 U}{\partial r^2} \qquad (5)$$

and

$$\begin{aligned} U(r, o) &= rC_i \\ U(o, t) &= O \qquad (6) \\ U(R, t) &= RC_s^*(t) \end{aligned}$$

The solution to this problem and consequently to the original set out in Equations (2) and (3) is

$$C_s(r, t) - C_s^*(t) = \frac{2R}{\pi r}\int_0^t \frac{dC_s^*(\phi)}{d\phi} \cdot \sum_1^\infty (-1)^n \frac{\sin n\pi \frac{r}{R}}{n} \cdot \exp\left\{-\frac{Dn^2\pi^2}{R^2}(t-\phi)\right\} d\phi \qquad (7)$$

By definition

$$\frac{4}{3}\pi R^3 W(t) = \int_0^R 4\pi r^2 C_s(r, t)\, dr \qquad (8)$$

and so if one substitutes for $C_s(r, t)$ from (7) it is found that

$$W(t) = C_s^*(t) - \frac{6}{\pi^2}\sum_1^\infty \frac{1}{n^2} \cdot \exp\left\{-\frac{Dn^2\pi^2 t}{R^2}\right\}\int_0^t \frac{dC_s^*(\phi)}{d\phi} \cdot \exp\left\{\frac{n^2\pi^2 D\phi}{R^2}\right\} d\phi \qquad (9)$$

The time derivative of Equation (9), i.e., the rate equation for the dispersed phase, is

$$\frac{dW}{dt} = \frac{6D}{R^2}\sum_1^\infty \int_0^t \frac{dC_s^*(\phi)}{d\phi} \cdot \exp\left\{-\frac{n^2\pi^2 D(t-\phi)}{R^2}\right\} d\phi \qquad (10)$$

The numerical value of the terms of the exponential series in Equations (9) and (10) drops rapidly for large values of $n^2\pi^2 Dt/R^2$, and so the first term of the series adequately represents the function. Under these circumstances one may write for Equation (9)

$$W(t) = W^*(t) - \frac{6}{\pi^2}\int_0^t \frac{dC_s^*(\phi)}{d\phi} \cdot \exp\left\{-\frac{\pi^2 D}{R^2}(t-\phi)\right\} d\phi \qquad (11)$$

and for (10)

$$\frac{dW}{dt} = \frac{6D}{R^2}\int_0^t \frac{dC_s^*(\phi)}{d\phi} \cdot \exp\left\{-\frac{\pi^2 D}{R^2}(t-\phi)\right\} d\phi \qquad (12)$$

Eliminating the integral expression between Equations (11) and (12) leads to the conclusion for longer times or in general larger values of $\pi^2 Dt/R^2$ that

$$\frac{dW}{dt} = \frac{\pi^2 D}{R^2}(W^* - W) \qquad (13)$$

Further under these circumstances

$$ka = \frac{\pi^2 D}{R^2} \qquad (14)$$

As the dimensionless group $\pi^2 Dt/R^2$ decreases in value to the point where terms involving $n = 2, 3, \cdots$ become significant, then one must return to the use of rate equation (10) since (13) will fail under these circumstances. These conclusions are independent of the distribution relation between $C_s^*(t)$ and its continuous-phase counterpart, as this distribution relation has not been used in the derivation.

LITERATURE CITED

1. Wicke, E. von, *Kolloid Z.*, **93**, 139 (1940).