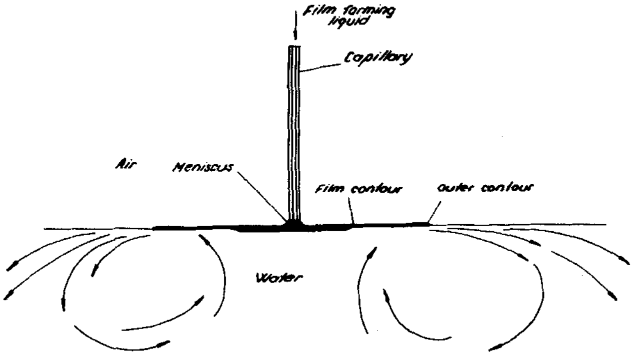

Fig. 7. Flow pattern formed during the dissolving process of a film under the action of surface forces.

be assisted by the influence of the walls and bottom of the dish. On the other hand, near the film contour a certain suction is exerted on the bulk liquid (by the rapid moving free surface), so that the bulk liquid moves upward below the film, to be eventually swept along by the surface layer. After a certain time, a steady toroidal motion pattern is developed (Figure 7). If the free surface is contaminated by surface active agents, this toroidal motion becomes more evident, since the moment the moving surface reaches the outer contour, it is deflected below the stagnant film. The movement continues beneath this stagnant film but the horizontal velocity components are reduced more quickly, resulting in a more marked downward motion.

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LITERATURE CITED

1. Brückner, R., *Naturwiss.*, **47**, 371, 372 (1960).
2. Jebsen-Marwedel, H., *Chem. Z. Chem. App.*, **90**, 393 (1966).
3. Kroepelin, H., and H. J. Neumann, *Naturwiss.*, **43**, 347 (1956); **44**, 304 (1957).
4. Langmuir, I., and O. B. Langmuir, *J. Phys. Chem.*, **31**, 1719 (1927).
5. Linde, H., *Fette, Seifen, Anstrichmittel*, **60**, 1053 (1958).
6. ———, and K. Winkler, *Z. Phys. Chem.*, **225**, 223 (1964).
7. Maroudas, N. G., and H. Sawistowski, *Chem. Eng. Sci.*, **19**, 919 (1964).
8. Marwedel, G., and H. Jebsen Marwedel, *Farbe Lack*, **67**, 276 (1961).
9. Merson, R. L., and J. A. Quinn, *AIChE J.*, **11**, 391 (1965).
10. Olander, D. R., and L. B. Reddy, *Chem. Eng. Sci.*, **19**, 67 (1964).
11. Orell, A., and J. W. Westwater, *AIChE J.*, **8**, 350 (1962).
12. Ruckenstein, E., and C. Berbente, *Chem. Eng. Sci.*, **19**, 329 (1964).
13. Sawistowski, H., and G. E. Goltz, *Trans. Inst. Chem. Engrs.*, **41**, 174 (1963).
14. Sigwart, H., and H. J. Nassenstein, *Naturwiss.*, **42**, 459 (1955); *Z. Ver. Dtsch. Ing.*, **98**, 543 (1956).
15. Skogen, A., *Am. J. Phys.*, **26**, 25 (1958).
16. Sternling, C. V., and L. E. Scriven, *AIChE J.*, **5**, 514 (1959).
17. Volpicelli, G., and Leopoldo Massimilla, *Chim. Ind.*, **45**, 405 (1963).
18. Zuiderweg, F. J., and A. Harmens, *Chem. Eng. Sci.*, **9**, 89 (1958).

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An Improved Version of the Rate Equation for Molecular Diffusion in a Dispersed Phase

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A frequency domain analysis of reversible molecular diffusion in a granule or relatively stagnant drop of fluid reveals that for the larger values of time the rate equation reduces to

$$\frac{dW}{dt} = \frac{15D}{R^2}(W^* - W)$$

Compared with an earlier time domain result

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

the rate predicted is $15/\pi^2 = 1.516$ greater and this has been confirmed by results of experiment. An analysis of time constants shows that the dimensionless group relation

$$\frac{Dt}{R^2} \geqq 0.101$$

defines mathematically that which is meant by the larger value of time limitation.

Some time ago it was observed that clarification appeared to be desirable for the rate equation for reversible molecular diffusion within a dispersed phase such as a granular solid or a relatively stagnant drop of fluid (2). This was based on the fact that in the periodical literature one frequently finds the assumption that

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

At that time it was shown that the governing differential equation for diffusion in an equivalent sphere of dispersed phase, which is

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

could be solved subject to the limiting conditions

$$C_s(r,o) = C_i, \text{ a constant} \quad (3)$$

$$C_s(o,t) = \text{ a maximum or minimum} \quad (4)$$

$$C_s(R,t) = C_s^*(t) \quad (5)$$

to show that the rate equation is

$$\frac{dW}{dt} = \frac{6D}{R^2} \sum_1^\infty \int_o^t \frac{dC_s^*(\phi)}{d\phi} e^{\frac{-n^2\pi^2 D(t-\phi)}{R^2}} d\phi \quad (6)$$

For data analysis or subsequent simultaneous solution with other mathematical expressions, this equation is cumbersome. Simplified versions are of interest as are also the restrictions on the assumed form given by Equation (1). For large values of time the first term of the series dominates both this rate equation and the concentration distribution from which it was derived. After some mathematical manipulation it was shown for this long time case that the rate equation simplifies to

$$\frac{dW}{dt} = \frac{\pi^2 D}{R^2} (W^* - W) \quad (7)$$

Thus for this special case one can show by comparison the physical composition of ka, that is

$$ka = \frac{\pi^2 D}{R^2} \quad (8)$$

Equation (7) could for reference sake be referred to as the long time 'time domain' approximation to Equation (6).

In Equation (6) the ratio of the first to the second or subsequent time constants is four or more. Thus in the first term by the time

$$\frac{n^2\pi^2 Dt}{R^2} = \frac{\pi^2 Dt}{R^2} \geqq 1; \; t \geqq \text{one time constant}$$

we have in all subsequent terms

$$\frac{n^2\pi^2 Dt}{R^2} \geqq 4; \quad n = 2,3, \; \ldots .$$

In the field of automatic control it is an established fact that a transfer function containing more than one time constant is dominated by one time constant if that one is at least four to five times greater than all others. Since this is the case at hand it is concluded that larger values of time means

$$\frac{Dt}{R^2} \geqq \frac{1}{\pi^2} = 0.101$$

During some recent investigations of diffusion phenomena it was found that treatment of these problems in the frequency domain leads to a small but significant difference in Equation (7). In view of the importance of Equation (1), it appears worthwhile to report this fact via that which follows.

THE IMPROVED RATE EQUATION

The substitution

$$U(r,t) = r\, C_s(r,t) \quad (9)$$

converts Equation (2) to

$$\frac{\partial U}{\partial t} = D \frac{\partial^2 U}{\partial r^2} \quad (10)$$

and limiting condition Equations (3) to (5) become

$$U(r,0) = rC_i \quad (11)$$

$$U(0,t) = 0 \quad (12)$$

$$U(R,t) = RC_s^*(t) \quad (13)$$

If one now defines

$$g = \delta_t U = p \int_0^\infty e^{-pt}\, U(r,t)\, dt \quad (14)$$

$$h^* = \delta_t C_s(t) \quad (15)$$

then by the method of Laplace transform one can show that the transform solution to Equation (10) to (13) is

$$g - rC_i = R(h^* - C_i) \frac{\sinh \sqrt{\frac{p}{D}}\, r}{\sinh \sqrt{\frac{p}{D}}\, R} \quad (16)$$

By definition

$$W = \frac{\int_o^R 4\pi r^2 C_s(r,t) dr}{\frac{4}{3}\pi R^3} = \frac{3}{R^3} \int_o^R r^2 C_s(r,t) dr \quad (17)$$

Thus if

$$w = \delta_t W \quad (18)$$

then

$$w = \frac{3}{R^3} \int_o^R r\, g\, dr \quad (19)$$

Substitution for g in this equation with Equation (16) reveals after rearrangement that

$$p(w - C_i) = \frac{3D}{R^2} \frac{(h^* - C_i)}{R^2} \frac{\theta \cosh \theta - \sinh \theta}{\sinh \theta} \quad (20)$$

where

$$\theta = \sqrt{\frac{p}{D}}\, R \quad (21)$$

Solving Equation (20) for C_i and using this result to eliminate C_i only from the right-hand side of Equation (20) we get the result that

$$p(w - C_i) = \frac{3D}{R^2} (w^* - w) \frac{\theta^2(\theta \cosh \theta - \sinh \theta)}{3(-\theta \cosh \theta + \sinh \theta) + \theta^2 \sinh \theta} \quad (22)$$

since

$$w^* = \frac{3}{R^3} \int_o^R r^2 \delta_t C_s^*(t) dr = h^* \quad (23)$$

Although it may not be recognizable as such rate Equation (22) is the Laplace transform of Equation (6).

The final value theorem may be used to determine the large time $\left(\frac{Dt}{R^2} \geqq 0.101\right)$ counterpart of Equation (22). Thus as $t \to \infty$, $p \to 0$ and consequently $\theta \to 0$. As $\theta \to 0$ in Equation (22) the right hand side becomes indeterminate. Applying l'Hospitals rule twice, one finds that

$$p(w - C_i) = \frac{3D}{R^2} (w^* - w) \left(4 + \frac{\theta}{\tanh \theta}\right) \quad (24)$$

which in the limit reduces to

$$p(w - C_i) = \frac{15D}{R^2} (w^* - w) \quad (25)$$

The inverse transform is

$$\frac{dW}{dt} = \frac{15D}{R^2} (W^* - W) \quad (26)$$

Rate Equation (26) is the long time frequency domain approximation to Equation (6). It will be noted that it differs from the long time 'time domain' approximate Equation (7) by a factor

$$\frac{15}{\pi^2} = 1.516$$

Thus Equation (7) is in error by exactly this factor as t approaches infinity. Both Equations (7) and (26) state that for sufficiently large t, the rate of molecular diffusion in the granule becomes proportional to the difference between the amount that has been sorbed W and that which can be sorbed W^*. For all practical purposes that which has been said here applies for all t determined by the relation.

$$\frac{Dt}{R^2} \geqq 0.101$$

It should be noted that after having stated the problem in Equations (2) to (5) [or (9) to (13), their equivalent] pure mathematics leads to Equation (26) for the larger values of time. No other postulates, assumptions, or experimental data are required to reach this conclusion.

EXPERIMENTAL EVIDENCE FAVORING THE IMPROVED RATE EQUATION

Glueckauf (*1*), in citing some previous experimental work, recommends for the conditions under consideration that in Equation (1) the value of the constant be taken as

$$\text{Constant} = \frac{14D}{R^2}$$

During the course of his paper more data are analyzed to test four empirical rate equations to show that the number 14 is closer to being 15. Also Equation (1) is most acceptable for reversible kinetics involved here. This obviously tends to substantiate the findings reported as Equation (26), particularly when the difficulties of experimental work are considered.

DISCUSSION

Equation (6) and the concentration distribution equation from which it was derived can be integrated by parts and then after some mathematical manipulation all in the time domain it can be shown that

$$\frac{dW}{dt} = \frac{\pi^2 D}{R^2}(W^* - W) + (A_1 - A_2)\frac{6}{\pi^2}\frac{dW^*}{dt} - (A_2 - A_3)\frac{6R^2}{\pi^4 D}\frac{d^2W^*}{dt^2} + \text{etc.} \quad (27)$$

where

$$A_p = \sum_1^\infty \frac{1}{n^{2p}} - \sum_1^\infty \frac{e^{\frac{-n^2\pi^2 Dt}{R^2}}}{n^{2p}} \quad (28)$$

Glueckauf pointed out that if W^* is not an exponential function this series converges rapidly. Also

$$A_p - A_{p+1} \rightarrow \sum_1^\infty \frac{1}{n^{2p}} - \sum_1^\infty \frac{1}{n^{2p+2}}$$

if

$$\frac{Dt}{R^2} > 0.1$$

Although he did not state how the latter restriction came about, it is quite obvious from the time constant analysis presented earlier in this paper that there is agreement with it. Thus

$$\frac{dW}{d\epsilon t} = \pi^2(W^* - W) + \underbrace{\left(1 - \frac{\pi^2}{15}\right)}_{0.342}\frac{dW^*}{d\epsilon t} - \underbrace{\left(\frac{1}{15} - \frac{2\pi^2}{315}\right)}_{0.0040}\frac{d^2W^*}{d(\epsilon t)^2} + \text{etc.} \quad (29)$$

where

$$\epsilon = \frac{D}{R^2}$$

After dropping the terms involving derivatives of W^* of order greater than one and assuming that

$$\frac{dW^*}{d\epsilon t} = \frac{dW}{d\epsilon t} \quad (30)$$

he was lead to a result consistent with his experiments and which is also consistent with that given by Equation (26). The dropping of derivatives as well as approximate Equation (30) is open to obvious criticism unless one considers that with the benefit of experimental results one can see by inspection of Equation (29) at least one way to obtain Equation (1) in a form consistent with experiment. One therefore cannot quarrel with the modest claim by Glueckhauf that his resulting rate equation was an empirical one.

CONCLUSIONS

For the diffusion postulated in Equations (2) to (5) and tested by Glueckhauf there appears to be little doubt that for

$$\frac{Dt}{R^2} \geqq 0.101$$

Equation (26), compared with (6), is the simplest rate equation possessing both utility and precision consistent with theory and experiment. Furthermore the exposition given in this paper proves that rate Equation (26) has a sound mathematical foundation once the problem is stated as in Equations (2) to (5) [or (9) to (13)] and solved for the larger values of time. No gimmicks are required to arrive at Equation (26) and this is in contrast to previous work reported in the literature.

From an academic viewpoint Equation (29) is of interest because, as one would expect, it complicates data analysis as does Equation (6). Both equations are time domain expressions and present the same order of difficulty in determining the asymptotic rate equation for long times and in the absence of experimental data. It is not difficult, for example, to concoct the theoretical argument that for long time operation of a percolation operation that

$$\frac{dW^*}{dt} \rightarrow 0$$

and Equation (29) therefore reduces to Equation (7). Perhaps we are to learn from this that the frequency domain has the advantage of compacting into a closed expression a function which in the time domain contains an infinite number of terms. Also, the final value theorem can be applied in the frequency domain to produce a useful result, whereas this is not true in the time domain and specifically for the problem at hand. To this extent the final value theorem applied in the frequency domain provides the same additional piece of information required of experiment in the time domain.

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NOTATION

C_s = concentration of a solute in a sphere at location r,t, mole/cu. ft.
constant in Eq. 1 = *ka* conventional nomenclature of chemical engineering, hr^{-1}.
D = molecular diffusivity of mass, sq. ft./hr.
r = radial position in sphere, ft.
R = radius of sphere, ft.
t = time, hr.
W = average concentration of a solute in a dispersed phase, mole/cu.ft.
W^* = average interface concentration on the dispersed phase side of the interface between dispersed phase and continuous phase, mole/cu. ft.

LITERATURE CITED

1. Glueckauf, E., *Trans. Faraday Soc.*, **51**, 1540 (1955).
2. Jury, S. H., *AIChE J.*, 3, 8J (June, 1957).

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