The solution of Equation (1) with conditions (3) has been given by Carslaw and Jaeger (5) and is

$$u(y,t) = \frac{g}{\nu M^2}\left[I - \frac{\cosh M(y\text{-}h)}{\cosh Mh} \right]$$

$$-\frac{16\, gh^2}{\pi\nu} \sum_{n=1}^{\infty} \frac{e^{-\left(M^2 + \frac{\lambda_n{}^2\pi^2}{4h^2} \right)\nu t}}{\lambda_n(\lambda_n{}^2\pi^2 + 4\, M^2h^2)} \times \sin\frac{\lambda_n\pi y}{2h} \qquad (5)$$

where $M^2 = \sigma B_o{}^2/(\rho\nu)$, $\lambda_n = 2n - 1$.

Integrating (5) over the film thickness gives the flow rate

$$q = \int_0^h u\, dy$$

$$= \frac{g}{\nu M^2}\left(h - \frac{\tanh Mh}{M} \right)$$

$$-\frac{32\, g\, h^3}{\pi^2\nu} \sum_{n=1}^{\infty} \frac{e^{-\left(M^2 + \frac{\lambda_n{}^2\pi^2}{4h^2} \right)\nu t}}{\lambda_n{}^2\, (\lambda_n{}^2\pi^2 + 4\, M^2h^2)} \qquad (6)$$

Combining (6) with (2) and (4) we get

$$x = \frac{gt \tanh^2 Mh}{\nu M^2} + \frac{64\, g\, h^2}{\pi^2\nu^2} \sum_{n=1}^{\infty} \frac{e^{-\left(M^2 + \frac{\lambda_n{}^2\pi^2}{4h^2} \right)\nu t}}{\lambda_n{}^2(\lambda_n{}^2\pi^2 + 4\, M^2h^2)^3}$$

$$[10\, \lambda_n{}^2\pi^2h^2 + \lambda_n{}^4\pi^4\nu t + 4h^2M^2(2h^2 + \lambda_n{}^2\pi^2\nu t)] \qquad (7)$$

The limiting case $M \rightarrow 0$ has been found to agree with the results given by Gutfinger and Tallmadge (2).

Further, for large values of time, the flow rate and the film thickness become

$$q = \frac{g}{\nu M^2}\left(h - \frac{\tanh Mh}{M} \right) \qquad (8)$$

and

$$x = \frac{g\, t}{\nu}\left(\frac{\tanh Mh}{M} \right)^2 \qquad (9)$$

Identical results are obtained for large values of M.

Since from (9), $dh/dM = (\sinh 2Mh - 2Mh)/2M^2$ and is positive for all M and h, the film thickness h increases with the increase in M for any given x and t. Therefore, it may be concluded that the fall of the film can be delayed by using hydromagnetic effects.

NOTATION

B_o = applied magnetic field in the y direction
g = gravitational acceleration
h = thickness of the liquid film
M = $B_o(\sigma/(\rho\nu))^{1/2}$
q = flow rate per unit width
t = time
u = velocity in the x direction
x = vertical coordinate in the downward direction
y = coordinate measured along the perpendicular to the plane of the wall

Greek Letters

μ = dynamic viscosity
ρ = density
ν = kinematic viscosity
σ = electrical conductivity

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A Heat Transfer Analogy for Diffusion and First-Order Chemical Reaction in a Catalyst Pore

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The expressions for rate of reaction in a catalyst pore can be expressed neither in terms of simple additive resistances nor by means of a simple kinetic rate law proportional to catalyst surface area. However, a rather thorough-going analogy exists between a first-order reaction in a catalyst pore and heat transport to a surrounding fluid from a longitudinal fin on a heated tube. This analogy extends not only to catalytic and heat transfer efficiency, but also to the nonlinear dependence of rate on transfer area and to the correspondence that exists between catalyst poisoning and fouling of a heat transfer surface.

For an idealized cylindrical catalyst pore the usual boundary conditions rest upon taking the fluid composition at the pore mouth equal to that of the bulk fluid phase, C_1 and assuming zero concentration gradient at the bottom of the pore. The steady state concentration distribution for this situation is

$$\frac{C(x)}{C_1} = \frac{\cosh\,[\lambda_c(L - x)]}{\cosh\,(\lambda_c L)} \qquad (1)$$

The corresponding case of an idealized longitudinal tube fin, the base of which is maintained at temperature T_1 with a vanishingly small heat transfer rate at the tip of the fin, requires a steady state temperature distribution:

$$\frac{T(x) - T_o}{T_1 - T_o} = \frac{\cosh[\lambda_T(L-x)]}{\cosh(\lambda_T L)} \tag{2}$$

The formal analogy between Equations (1) and (2) is clear. This formulation accounts only for transport along the long axis of the pore or fin. Resistance to transfer in the transverse direction has been neglected, as is usual for narrow pores and thin fins.

ASYMPTOTIC BEHAVIOR FOR LONG PORES AND LONG FINS

The rate of chemical reaction on the wall of the pore is equal to the rate of diffusion of reactant into the pore as given by Fick's Law at the mouth of the pore:

$$\begin{aligned} J &= -DA_p \left.\frac{dC}{dx}\right)_{x=0} \\ &= DA_pC_1\lambda_c \tanh(\lambda_c L) \end{aligned} \tag{3}$$

Likewise, the rate of heat transfer from the fin is given by Fourier's Law at the base of the fin:

$$\begin{aligned} Q &= -k_TA_f \left.\frac{dT}{dx}\right)_{x=0} \\ &= k_TA_f\,(T_1 - T_o)\lambda_T \tanh(\lambda_T L) \end{aligned} \tag{4}$$

For very short pores or fins the hyperbolic tangent can be approximated by its argument, and equations (3) and (4) take the conventional form

$$J = k_cA_sC_1 \tag{5}$$

and

$$Q = h_fA_s\,(T_1 - T_o) \tag{6}$$

For a very long pore or fin tanh $(\lambda L) \approx 1$ and the rates are given by

$$J = \sqrt{P_pA_pDk_c}\;\; C_1 \tag{7}$$

$$Q = \sqrt{P_fA_fk_Th_f}\;\; (T_1 - T_o) \tag{8}$$

Whether a pore or fin behaves as though it is long or short is uniquely described by $\lambda_T L$ or $\lambda_c L$. When this product is greater than about 2, the pores or fins behave as though they are long. The product must be less than about 0.1 for the pores or fins to behave as though they are short.

EFFECTIVENESS FACTOR AND EFFICIENCY

From the development above it becomes apparent that the unavailable surface area for a first-order reaction in a catalyst pore is entirely analogous to the ineffective fin area in the case of heat transfer from a tube fin. This can be developed formally in terms of the catalyst *effectiveness factor* and the fin *efficiency factor*. The effectiveness factor is defined as the actual reaction rate divided by the rate that would be observed if the entire surface of the pore wall were available. From Equation (3)

$$\begin{aligned} E.F. &= \frac{DA_p\,C_1\,\lambda_c \tanh(\lambda_c L)}{2\pi r L k_c C_1} \\ &= \frac{\tanh(\lambda_c L)}{\lambda_c L} \end{aligned} \tag{9}$$

The fin efficiency can be similarly defined as the ratio of the actual heat transfer rate to the rate that would be obtained if the entire fin surface were at temperature T_1, (that is, *available* in catalyst terminology). From Equation (4)

$$\begin{aligned} \text{Fin Efficiency} &= \frac{k_TA_f\,(T_1 - T_o)\,\lambda_T \tanh(\lambda_T L)}{h_fA_s\,(T_1 - T_o)} \\ &= \frac{\tanh(\lambda_T L)}{\lambda_T L} \end{aligned} \tag{10}$$

The analogy between Equations (9) and (10) is obvious.

It is also interesting to note that the catalyst effectiveness factor and the fin efficiency can also be defined in terms of driving-force ratios with identical results. Thus the catalyst effectiveness factor is also equal to the ratio of the mean reactant concentration within the pore to the concentration at the mouth of the pore

$$E.F. = \frac{\overline{C}}{C_1} = \frac{\tanh(\lambda_c L)}{\lambda_c L} \tag{11}$$

where

$$\overline{C} \equiv \frac{1}{L}\int_o^L C(x)\,dx$$

with $C(x)$ given by Equation (1). Similarly, the tube-fin efficiency factor is equal to the mean-temperature driving force along the length of the fin divided by the maximum-temperature driving force at the base of the fin:

$$\text{Fin Efficiency} = \frac{\overline{(T - T_o)}}{T - T_o} = \frac{\tanh(\lambda_T L)}{\lambda_T L} \tag{12}$$

where

$$\overline{(T - T_o)} \equiv \frac{1}{L}\int_o^L (T(x) - T_o)\,dx$$

with $(T(x) - T_o)$ given by Equation (2). For a thorough treatment of fin efficiency and heat transfer from finned tubes the reader is referred to Gardner (*2*).

Poisoning and Fouling

In catalyst poisoning, a part of the surface is rendered ineffectual for catalytic reaction by the adsorption of a so called "poison." The analogous situation for a heat transfer fin is surface fouling if the interfering deposit possesses an extremely small thermal conductivity. When the poisoning or fouling is homogeneous, the entire surface is uniformly affected by some fractional coverage, α, of poison or deposit. This situation is described by simply substituting $k_c(1 - \alpha)$ for the intrinsic reaction rate constant in the case of the catalyst and $h_f(1 - \alpha)$ for the fluid-side heat transfer coefficient in the case of the fin. For the catalyst pore the fraction of activity remaining after poisoning is given by

$$\begin{aligned} F &= \frac{\text{reaction rate poisoned}}{\text{rate unpoisoned}} \\ &= \frac{DA_pC_1\sqrt{1-\alpha}\,\lambda_c \tanh[\lambda_c L\sqrt{1-\alpha}]}{DA_pC_1\lambda_c \tanh(\lambda_c L)} \\ &= \sqrt{1-\alpha}\;\frac{\tanh(\lambda_c L\sqrt{1-\alpha})}{\tanh(\lambda_c L)} \end{aligned} \tag{13}$$

The corresponding result for the tube fin is

$$F = \sqrt{1-\alpha}\;\frac{\tanh(\lambda_T L\sqrt{1-\alpha})}{\tanh(\lambda_T L)} \tag{14}$$

For (λL) small (short pores or fins), Equations (13) and (14) reduce to

$$F \cong 1 - \alpha \quad \text{for} \quad (\lambda L) < 0.1 \tag{15}$$

For (λL) large (long pores or fins), these equations reduce to

$$F \cong \sqrt{1 - \alpha} \quad \text{for} \quad (\lambda L) > 2 \tag{16}$$

Equations (15) and (16) hold for either tube fins or catalyst pores. With respect to Equation (16) for long pores or fins the reason that the catalytic activity, or heat transfer effectiveness, falls off more slowly than linearly with surface poisoning or fouling is that the surface is not uniformly efficacious when the pore is deep or the fin is long. Although the deeper regions of the pore and the outer part of the fin may be poisoned or fouled to the same extent as other parts of the surface, these extremities are less effective than the rest of the surface, and changing the nature of these parts of the surface does not produce a proportionate effect.

The effect of poisoning is interesting and extraordinary when the poison is strongly adsorbed in an immobile condition near the mouth of the pore. The analogous situation for the heat transfer fin is deposition at the base of the fin. In either case, the corresponding surface of the catalyst pore or tube fin becomes ineffective. Then the chemical reactant must diffuse more deeply into the pore before it can react, and thermal energy must be conducted further along the fin before it can pass into the surrounding fluid. Either situation is described by

$$F = \frac{\tanh[\lambda L(1-\alpha)]}{1 + \alpha L \lambda \tanh[\lambda L(1-\alpha)]} \cdot \frac{1}{\tanh(\lambda L)} \tag{17}$$

or

$$F = \frac{1}{1 + \alpha \lambda L} \quad \text{for} \quad \lambda L(1-\alpha) > 2 \tag{18}$$

Here α is the fraction of catalyst-pore length or tube-fin length covered by poison at the pore mouth or fouling deposit at the base of the fin; thus the reactant must diffuse a distance αL into the pore before it can react, and thermal energy must diffuse a distance αL along the fin before it can pass through the fin surface into the surrounding fluid. Equation (18) predicts much more severe lowering of activity due to selective fouling or poisoning. The reason for this very fast fall of activity with surface coverage is that poisoning a catalyst pore mouth or fouling the base of a tube fin blocks the most effective part of the surface and forces the reactant or the thermal energy to diffuse farther before it can either react or pass to the fluid.

The foregoing equations are identical with those presented by Wheeler (*3, 4*) for porous catalysts; it is pointed out here that these equations apply equally well to heat transfer from fouled tube fins when α and λ are defined properly. It has been found experimentally (*5, 6*) that the first addition of poison often has a more pronounced effect than the final amounts, in accord with the prediction of Equation (18). One interpretation of this behavior is the poisoned-pore-mouth model outlined above and for which the heat transfer analogy is possible. An alternative explanation is that, of all the active sites distributed at random over the surface, the more active ones are poisoned first. Here the earlier poisoning singles out the more chemically active sites rather than those more accessible within a pore, and the heat transfer analogy does not apply. Actual catalyst poisoning probably involves aspects of both models.

No attempt has been made here to account for heat of reaction and the resulting temperature gradient [see Carberry (*7*)] in the catalyst since this would destroy the analogy. Neither does this analogy hold for catalytic reactions of intrinsic order other than one. The reason is that the analogy rests on a correspondence between the surface chemical reaction and heat transfer from the fin surface to a surrounding fluid. The latter is always a first order process unless thermal radiation is involved. Another shortcoming of the analogy is that tube fins are seldom designed so long that they possess significant ineffective transfer area, whereas the internal area of catalyst pellets commonly can be largely ineffective. The reason for this is that the rate of diffusion along a poisoned catalyst pore is often slower than the chemical reaction at the unpoisoned pore surface, whereas thermal conduction along a fouled metal fin is seldom slower than heat transfer from the unfouled surface to the surrounding fluid.

While the heat transfer analogy is possible for a first-order reaction in a cylindrical catalyst pore, it cannot be applied to catalyst selectivity for one of several parallel or consecutive reactions in which pore diffusion can play a significant role. Furthermore, it should be noted that a typical catalyst pore most certainly is not cylindrical and that more complex models have been proposed to account for interconnecting macro- and micropores (*8*). In spite of the shortcomings of the analogy, it is a useful aid to understanding and interpretation. The author has found it particularly useful in teaching students the rudiments of reaction kinetics as observed over porous catalysts.

NOTATION

A = cross-sectional area or surface area (with subscript s)
C = concentration of reactant in fluid phase
D = diffusion coefficient of reactant in catalyst pore
$E.F.$ = catalyst effectiveness factor
F = fraction of activity remaining after poisoning or fouling
J = rate of mass transport or rate of reaction
k_c = intrinsic rate constant per unit surface area for catalytic reaction
k_T = thermal conductivity of tube fin
L = length of catalyst pore or tube fin
P = perimeter of pore or fin
Q = rate of heat transport
r = radius of pore
T = temperature
x = distance measured along pore axis from its mouth or along fin axis from its base
α = fraction of transfer surface poisoned or fouled
$\lambda_c \equiv \sqrt{2k_c/r_pD}$
$\lambda_T \equiv \sqrt{h_fP_f/A_fk_T}$

Subscripts

o = temperature of fluid phase surrounding fin
1 = concentration at mouth of pore or temperature at base of fin
c = catalytic reaction
f = tube fin
p = catalyst pore
s = surface area
T = thermal energy transport

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