t_j assume such values as to minimize the production of entropy in the system.

The rate of entropy production per unit volume is $-(q''/T^2)$ grad T (*8*), where q'' is the heat flux and T the absolute temperature. Hence one may approximate ϕ, the entropy production per unit area, by

$$\phi = -\sum_{i=1}^{N} \frac{q_{i-1,i}''}{T_i^2}\left(\frac{T_i - T_{i-1}}{\Delta x}\right)\Delta x \qquad (1)$$
$$= \frac{k}{\Delta x}\sum_{i=1}^{N}\left(\frac{t_i - t_{i-1}}{T_i}\right)^2$$

where k is the thermal conductivity, Δx the thickness of each layer, and t the temperature in degrees centigrade or Fahrenheit. Assuming that $|t_N - t_0| \ll T_0$, one may write

$$\Phi \equiv \frac{(\Delta x)T^2\phi}{k} \cong \sum_{i=1}^{N} (t_i - t_{i-1})^2 \qquad (2)$$

The problem now reduces to minimizing Φ.

If one differentiates with respect to t_j and chooses a new value t_j^* to minimize Φ with respect to this variable, one finds

$$t_j^* = \frac{t_{j+1} + t_{j-1}}{2} \qquad (3)$$

Corresponding to t_j^* is a new Φ^* such that [with the help of Equation (3)]

$$\Phi - \Phi^* = (t_{j+1} - t_j)^2$$
$$+ (t_j - t_{j-1})^2 - (t_{j+1} - t_j^*)^2$$
$$- (t_j^* - t_{j-1})^2$$
$$= -2(t_j - t_j^*)$$
$$\cdot[t_{j+1} + t_{j-1} - (t_j + t_j^*)]$$
$$= (-2t_j + t_{j+1} + t_{j-1})$$
$$\cdot\left(\frac{t_{j+1} + t_{j-1}}{2} - t_j\right)$$
$$\therefore \quad \Phi^* - \Phi = -\frac{r_j^2}{2} \qquad (4)$$

where

$$r_j \equiv t_{j+1} + t_{j-1} - 2t_j \qquad (5)$$

To minimize Φ one may now choose the point with the greatest r_j (or one of such points if the r_j's are equal for several j) and apply Equation (3); new r_j's may then be computed and the process repeated. One now notes that the r_j's are identical with the residuals in the relaxation method and that this procedure is identical with the basic one-dimensional relaxation procedure.

To show that this process converges to the desired solution one first notes that Φ, as defined by Equation (2), is positive definite and hence has a lower bound of zero. Furthermore Equation (4) shows that Φ must decrease in each step of the process. It follows that Φ must approach a unique limit Φ_{min}. Hence for any prescribed $\epsilon^2/2$, $\epsilon > 0$ there must be a stage in the relaxation process after which $\Phi - \Phi^* < \epsilon^2/2$. It follows from Equation (4) that $|r_j| < \epsilon$, which completes the convergence proof. The analysis is readily extended to two or three dimensions.

When the temperature difference is not small compared with the absolute temperature, the interpretation is somewhat more complicated, although the steady state solution is still a state of minimum entropy production. In any case the relaxation procedure may also be considered as a minimization of the thermal dissipation function defined by Biot (*9*).

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Heat Transfer

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The comments of Leva and Wen* concerning the exclusion of the data of Van Heerden, et al., in working up the external surface correlation are appreciated. However, we wish to make the following comments.

While these data were not treated because of a lack of bed density (or fraction solids) values, we were of course aware that methods were available for estimating these quantities and that these methods need to be used for applying the correlation. However it was not felt that the large amount of time required for estimating bed voidages for the many Van Heerden runs could be justified, at the expense of working on the other data used, because of the limited usefulness of the Van Heerden data. While it is true that they represent a careful study of many variables and cover a wide range, all the work was done at a single and very low value (1.18) of L_H/D_T. Since the later studies of Van Heerden (cited in our paper) appear to show a strong and complex L_H effect in the region of low L_H/D_T, it was felt that conclusions resulting from the use of these data would be less profitable than those resulting from the study of data at higher L_H/D_T

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*A.I.Ch.E. Journal, 5, No. 1, 7M (1959).

values and data at low and varying L_H/D_T (Dow and Jakob). Furthermore the Van Heerden study was the only one in the external surface study that had only part of the bed in contact with the heat transfer surface, and there was thus an apparatus geometry difference between that study and all the others used.

The Van Heerden data should be studied however, and we have been gradually working them up since the publication of our paper. Our calculations confirm the deviations cited by Leva and Wen and point up the complexity of the low L_H/D_T region in the case of external surface. Our paper points out that the external surface correlation is uncertain in the low L_H/D_T region, and it is hoped that further studies will enable us to improve it in this region.

As to the differences in slope between curves of Van Heerden data and the external surface correlation curve, mentioned by Leva and Wen, we believe these to be caused not by an improper incorporation of the functional relationship between fluid mass velocity and bed expansion but by the uncertainty of the slope of the correlation curve in the low Reynolds number region resulting from the very small number of points in that region.

The differences in form between our external and internal surface correlations are indeed substantial but were found necessary in our empirical study. However it may still be hoped that more work in this field by others will yet produce a definitive correlation, theoretically based and covering in a single expression both external and internal surface operation.

Diffusion in a Pore of Irregular Cross Section—a Simplified Treatment

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In a recent issue of this journal Petersen* developed an expression for the convergence factor for diffusion through a pore whose cross section varied periodically along its length in a hyperbolic fashion, from which he demonstrated how the effective diffusivity in such a pore varied with the ratio of maximum to minimum cross-sectional area. This writer has had occasion to grapple with this same problem; by means of a very elementary analysis of the diffusion process and with the aid of some simplifying assumptions, he has developed a relation between the effective diffusivity and pore geometry that is in remarkably close agreement with Petersen's far more elegant analysis.

Consider two cylindrical capillaries, one of radius r_1 and length l_1 and the other of radius r_2 and length l_2, which are connected in series. An irregular pore may be considered as composed of any number of these characteristic units in series. Since the diffusional resistance offered by any one of these units is the same as any other, it is possible by characterizing the unit to characterize thereby the entire pore.

A component is assumed to be diffusing through this unit at steady state. If entrance and exit effects at the juncture of the two capillaries are neglected, the flux N through the two capillaries can be represented by

$$N = D(\pi r_1^2)\left(\frac{c_i - c'}{l_1}\right) = D(\pi r_2^2)\left(\frac{c' - c_0}{l_2}\right) \qquad (1)$$

If one defines two dimensionless ratios $L = l_1/l_2$ and $R = r_1/r_2$, Equation (1) can be solved for c' and the flux expressed in terms of the inlet and outlet concentration:

$$N = D\left(\frac{\pi r_1^2}{l_1}\right)(c_i - c_0)\left[\frac{L}{R^2 + L}\right] \qquad (2)$$

An equivalent uniform cylindrical pore can be defined as one with an average volume per unit length that is the same as that of the irregular pore*; that is,

$$\pi r_e^2(l_1 + l_2) = \pi r_1^2 l_1 + \pi r_2^2 l_2^2 \qquad (3)$$

The flux through the irregular pore can be equated to that through the equivalent pore, if an effective diffusivity is substituted for the diffusion coefficient.

$$N = D_e(\pi r_e^2)\,\frac{c_i - c_0}{l_1 + l_2} \qquad (4)$$

Substituting Equation (3) into (4) and equating the resulting relation to Equation (2), one finds that

$$D/D_e = \left[1 + \frac{L}{(L+1)^2}\cdot\left(\frac{R^2 - 1}{R}\right)^2\right] \qquad (5)$$

Equation (5) permits calculation of the convergence factor D_e/D as a function of R and L. The parameter R alone (or more correctly, R^2) appears in Petersen's derivation, since his assumed hyperbolic variation of pore cross section with length makes (L) and (R) interdependent.

In Figure 1 (D_e/D) is plotted as a function of R for various values of L. The dotted line on the graph represents Petersen's correlation. It will be noted that the two correlations are in rather close agreement for values of R up to about five, irrespective of the value of L. At higher values of R however they diverge appreciably. In view of the fact that with Petersen's hyperbolic construction of the pore the fraction of the pore length containing the bulges increases with the ratio of maximum to minimum pore diameter (that is, L increases with R), the observed divergence of the two correlations at high values of R is to be expected

In the absence of specific microscopic information about pore geometry, it is convenient to assume some arbitrary relation between L and R in order to express the convergence factor in terms of a single geometric parameter. One not unreasonable assumption is that the length of a bulge or constriction is proportional to its diameter, that is, that $L = R$. In this case Equation (5) becomes

$$D_e/D = \left[1 + \frac{(R-1)^2}{R}\right]^{-1} \qquad (6)$$

Equation (6) yields values of the convergence factor which are about 30% lower (at higher values of R) than Petersen's. In view of the simplifying assumptions employed in the present development this agreement is surprising. If Equation (5) is solved for the case

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*Petersen, E. E., *A.I.Ch.E. Journal*, 4, 343 (1958).

*Alternatively an equivalent cylindrical pore can be defined as one with a surface area per unit volume equal to that of the real pore; in this case the volume of the equivalent pore per unit length will be less than that of the real pore, and a number of equivalent pores in parallel must be selected such that the total pore volume per unit length is the same as that of the real pore. Since the diffusional flux through a uniform cylindrical pore is directly proportional to its cross-sectional area, these two definitions of the equivalent pore yield the same algebraic solution.